MIKHAYLOV, B.M.

USSR/ Chemistry - Biochemistry

Card 1/1 Pub. 40 - 17/26

Authors : Mikhaylov, B. M., and Blokhina, A. N.

Title : Photodehydrocondensation of anisole homologues. Photosynthesis of synestrol

Periodical : Izv. AN SSSR. Otd. khim. nauk 2, 323 - 325, Mar-Apr 1955

Abstract : The photochemical conversions of anisole homologues under the effect of ultraviolet rays and the presence of acetone were investigated. It was found that the parahomologues of anisole, when subjected to above mentioned conditions, experience photodehydrocondensation resulting in the formation of p-anisyl derivatives of aliphatic hydrocarbons. The very same process also led to the formation of synestrol from p-propylanisole. The products obtained during the reaction in the presence of benzophenone are described. Nine references: 4 German, 3 USA, 1 Italian and 1 USSR (1902-1949).

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Organ. Chem.

Submitted : June 17, 1954

MIKHAYLOV, B.M.; ARONOVICH, P.M.

Preparation of p-terphenyl. Izv.AN SSSR.Otd.khim.nauk no.5:945-946
S-O '55. (MLRA 9:1)

1.Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk
SSSR.

(Terphenyl)

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Structure and prop[er]ties of dimetal compounds of azomethines. I. Structure of metallic compounds of azomethines. B. M. Mikhailov and K. N. Kurdyumova. J. Gen. Chem. U.S.S.R. 25, 1087-9(1955)(Engl. translation).—See C.A. 50, 5[9]15. B. M. R.

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MIKHAYLOV, B.M.; KURDYUMOVA, K.N.

Structure and properties of azomethine dimetallic compounds. Part 1. Structure of azomethine metal compounds. Zhur.ob.khim. 25 no.9:1734-1737 S '55. (MIRA 9:2)
(Schiff bases)

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380

Complex lithium-aromatic compounds. N. G. Chernova and B. M. Mikhailov. *Zhur. Obshchei Khim.* 25, 2280-6 (1955). Treatment of 2 moles BuLi soln. in C_6H_6 with 1 mole fluorene in Et_2O gave after filtration and drying a yellow complex, $C_{13}H_9Li.2Et_2O$. Similarly, BuLi and 3-bromopyrene gave yellow $C_{16}H_9Li.Et_2O$. BuLi and fluorene in C_6H_6-dioxane gave yellow $C_{13}H_9Li.C_4H_8O_2$; 3-bromopyrene thus gave $2C_{16}H_9Li.3C_4H_8O_2$. BuLi in C_6H_6 treated with Ph_3Sb, and the mixt. heated and filtered, gave PhLi, which in dioxane-Et_2O gave $PhLi.C_4H_8O_2$, colorless; similarly formed was $1\text{-}C_{10}H_7Li.C_4H_8O_2$. Analysis is performed by hydrolysis and titration; dioxane is detd. by reaction with $HgCl_2$. All operations are run in N. G. M. Kosolapoff

Chem

MIKHAYLOV, B.M.; SHCHEGOLEVA, T.A.

Organo-boron compounds. Part 4. The synthesis of esters of dialkylboric acids using lithium reagents. Izv.AN SSSR Otd. khim.nauk 86 no.6:1124-1125 My '55. (MIRA 9:4)

1.Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR. (Boric acid)

Mikhaylov, B. M.

USSR/ Chemistry - Organic chemistry

Card 1/1 Pub. 22 - 30/62

Authors : Mikhaylov, B. M., and Vavor, V. A.

Title : Diphenylboric acid and its derivatives

Periodical : Dok. AN SSSR 102/3, 531-534, May 21, 1955

Abstract : Special experiments were made to prove that the statements of German chemists A. Michaelis (1894), and W. Koenig (1930) regarding the synthesis and properties of diphenylboric acid and its derivatives are false. It is the contention of the authors that the basic material and typo of reaction as described by the German scientists would rather have led to the formation of diaryl borates and not diphenylboric acid or diphenyl borates. The properties of diphenylboric acid and its derivatives as determined by this experiment prove beyond any doubt that the German chemistr did not deal with diphenylboric acid. Five German references (1894-1954).

Institutiin : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Organ. Chem.

Presented by: Academician B. A. Kazanskiy, January 11, 1955

MIKHAYLOV, B.M.

Relationship between the absorption spectra of clay dyed with methylene blue and the pH of the suspension. Dokl. AN SSSR 105 no.4:818-820 D '55. (MLRA 9:3)

1. Predstavleno akademikom D.V. Nalivkinym.
(Montmorillonite)

MIKHAYLOV, B.M.

Chem

Organoboron compounds. V. Preparation of [illegible] esters of phenylboric acid and diphenylboric acid with phenyllithium. B. M. Mikhailov and P. M. Aronovich. *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.* 1956, 311-14 (Engl. translation).—See *C.A.* 50, 11963*f*. VI. Action of phosphorus pentachloride on esters of diarylboron chlorides. Synthesis of diarylboron chlorides. B. M. Mikhailov and N. S. Fedotov. *Ibid.* 359. VII. Action of phosphorous pentachloride on esters of arylboric acids. Synthesis of esters of arylchloroboric acids. B. M. Mikhailov and T. V. Kostroma. *Ibid.* 361.—See *C.A.* 50, 11964*ab*. B. M. R.

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Organoboron compounds. V. Preparation of isobutyl esters of phenylboric acid and diphenylboric acid with the aid of phenyllithium. B. M. Mikhailov and P. M. Aronovich (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 322-6; cf. *C.A.* 50, 4817d, 11235c.—To (iso-BuO)$_2$BPhLi (6.28 g.) in 10 ml. H_2O was added 3 ml. 30% HCl and the mixt. repeatedly extd. with Et_2O, the ext. concd. and distd. with added H_2O to remove iso-BuOH, to yield on cooling 90% phenylboric acid, m. 207-10°; the aq. soln. was made alk. and concd., yielding after addn. of 20 ml. MeOH, careful neutralization and addn. of 2 g. $HgCl_2$, 7.8 g. boric acid as detd. by titration after addn. of mannitol. To PhLi soln. at −5° (from 17.3 g. PhBr, 1.6 g. Li, and 175 ml. Et_2O) was added 23 g. $B(OCH_2CHMe_2)_3$ in Et_2O with cooling finally to −60°; after 5 hrs. at −70° the mixt. was left in cold bath overnight and was then acidified with 20% HCl and extd. with Et_2O; the ext. was evapd., treated with H_2O and distd. to remove iso-BuOH, yielding 82% $PhB(OH)_2$. Similar reaction in which the reaction mass was satd. with dry HCl gave after filtration and distn. 68% *(iso-BuO)$_2$BPh*, b_4 116-17°, d_{20} 0.9243. To 77 ml. 1.3*N* BuLi in C_6H_6 in N atm. was added with ice cooling 11.5 ml. dry iso-BuOH and after cooling with ice the soln. of iso-BuOLi was treated with 26.2 g. iso-BuOBPh$_2$ in 50 ml. Et_2O; after 3 hrs. at 0° the mixt. was concd. *in vacuo* in N stream and the residue stirred with hexane gave 78% *Ph$_2$B(OBu-iso)$_2$Li* (I). This (15.9 g.) in 50 ml. Et_2O was treated with cooling with 20% HCl to acid reaction; the org. layer after evapn. was treated with isopentane, yielding 3.2 g. $PhB(OH)_2$ while the filtrate gave 27.8% iso-BuOBPh$_2$, b_4 142-5°. I in Et_2O treated 1 hr. with dry HCl gave 81.7% iso-BuOBPh$_2$ and 4.0% (iso-BuO)$_2$BPh. To Et_2O soln. of PhLi from 17.3 g. PhBr and 1.6 g. Li was added 21.4 g. (iso-BuO)$_2$BPh as above; after acidification with 20% HCl and distn. of 1/3

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Et_2O and iso-BuOH, the residue was fractionated yielding some Ph_3, 26.1% iso-$BuOBPh_2$ and 2.9 g. $(iso\text{-}BuO)_2BPh$. Reaction of equimolar mixt. of $(iso\text{-}BuO)_2BPh$ and PhLi as above followed by passage of dry HCl into the mixture, distn. of Et_2O, filtration of LiCl, washing with C_6H_6, distn. of C_6H_6 and iso-BuOH, and fractionation of the residue gave 5.5% $(iso\text{-}BuO)_2BPh$ and 71% iso-$BuOBPh_2$. VI. Action of phosphorus pentachloride on esters of diarylboric acids. Synthesis of diarylboron chlorides. B. M. Mikhailov and N. S. Fedotov. *Ibid.* 375-6.—To 20 g. Ph_2BOPr was added 18.6 g. PCl_5 (exothermic) and after distn. of PrCl and $POCl_3$, there was obtained 12.4 g. *Ph_2BCl*, b_8 119-20°, d_{20} 1.1037. Similarly 20 g. iso-$BuOB(C_{10}H_7\text{-}1)_2$ in 20 ml. C_6H_6 with 12.2 g. PCl_5 gave 12.6 g. *$(1\text{-}C_{10}H_7)_2BCl$*, $b_{0.4}$ 212-15°, in 70% yield. VII. Action of phosphorus pentachloride on esters of arylboric acids. Synthesis of esters of arylchloroboric acids. B. M. Mikhailov and T. V. Kostroma. *Ibid.* 376-7.—To 44.8 g. $PhB(OBu)_2$ was added 41.7 g. PCl_5 and after cessation of exothermic reaction the mixt. was distd., yielding BuCl, $POCl_3$, and 29.5 g. *$PhB(OBu)Cl$*, b_8 104-5°, d_{20} 0.9962, in 75% yield. Similarly 24.8 g. *$(iso\text{-}BuO)_2BC_6H_4Me\text{-}o$* and 20.8 g. PCl_5 gave 18.1 g. *$Cl(iso\text{-}BuO)BC_6H_4Me\text{-}o$*, b_{14} 114-15°, b_8 110-11°, d_{20} 0.9918, in 86% yield. VIII. Synthesis and properties of diarylboric acids. B. M. Mikhailov and V. A. Vaver. *Ibid.* 451-6.—To 0.5 mole $1\text{-}C_{10}H_7MgBr$ was added at −80° 0.225 mole $(iso\text{-}BuO)_3B$ and after 6-7 hrs. at −70°, the mixt. treated with 5% HCl, yielding on concn. of the org. layer 63% *$(1\text{-}C_{10}H_7)_2BOBu\text{-}iso$* (I), m. 104-5° (from hexane), after washing the residue with pentane; the wash liquid gave 15% *$1\text{-}C_{10}H_7B(OBu\text{-}iso)_2$*, b_8 166-8°, d_{20} 0.9777, which is hydrolyzed by atm. moisture. To 10 g. I in 20 ml. MeOH was added 15 ml. 30% NH_4OH, yielding

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after 0.5 hr. 97.5% $(1\text{-}C_{10}H_7)_2B(OH)_2NH_4$, m. 167–8° (from MeOH), which decomposes rapidly in air yielding NH_3, $C_{10}H_8$, and $1\text{-}C_{10}H_7BO_2H_2$. If this NH_4 salt in Et_2O was stirred with 1:1 HCl and the org. layer evapd. after 0.5 hr., there was obtained 71.7% $(1\text{-}C_{10}H_7)_2BOH$, m. 114.5–15° (from petr. ether), which heated *in vacuo* gave $C_{10}H_8$ and $1\text{-}C_{10}H_7B(OH)_2$. The above acid (2 g.) refluxed 2 hrs. with 5 ml. $SOCl_2$, concd. *in vacuo* and treated with C_6H_6-petr. ether, gave 98% $[(1\text{-}C_{10}H_7)_2B]_2O$, m. 190–2°. To 0.65 mole $p\text{-}BrC_6H_4MgBr$ (cf. Pink, *C.A.* 18, 668) was added over 0.5 hr. at −30° 0.25 mole $(iso\text{-}BuO)_3B$ in Et_2O and after 8 hrs. at −70° the mixt. was treated with 5% HCl, the org. layer concd. and the residue esterified with iso-BuOH; distn. gave 30% $(p\text{-}BrC_6H_4)_2BOBu\text{-}iso$ (II), b_2 161–3°, and 37% $p\text{-}BrC_6H_4B(OBu\text{-}iso)_2$, b_2 106–10°, d_{20} 1.1583. II (2.25 g.) shaken with 5 ml. 20% NH_4OH gave 87.3% $(p\text{-}BrC_6H_4)_2B(OH)_2NH_4$, m. 184–5° (from C_6H_6). II (1.23 g.) in 3.65 ml. 0.8N KOH was slowly distd. *in vacuo* at 70° under N giving a residue of 0.8 g. $(p\text{-}BrC_6H_4)_2B(OH)_2K$, crystals (from C_6H_6-MeOH). The NH_4 salt above with dil. HCl gave 88% $(p\text{-}BrC_6H_4)_2BOH$, m. 90–1° (from petr. ether), which forms similarly from the above K salt. Similarly, 0.6 mole $p\text{-}ClC_6H_4MgBr$ and 0.25 mole $(iso\text{-}BuO)_3B$ gave 40% $(p\text{-}ClC_6H_4)_2BOBu\text{-}iso$ (III), b_1 134–6°, d_{20} 1.1414, and 25% $p\text{-}ClC_6H_4B(OBu\text{-}iso)_2$, b_1 93–5°, d_{20} 1.0051; the former is rapidly oxidized in air, the latter is immediately hydrolyzed in moist air. III shaken with satd. $Ba(OH)_2$ gave 80.5% $(p\text{-}ClC_6H_4)_2B(OH)_2Ba$, insol. in H_2O, sol. in MeOH and EtOH. Shaken with 1:4 HCl it gave $(p\text{-}ClC_6H_4)_2B(OH)_2$, m. 76–8° (from aq. EtOH); it is decompd. by drying *in vacuo*, yielding PhCl and $p\text{-}ClC_6H_4B(OH)_2$. III with N NaOH gave $(p\text{-}ClC_6H_4)_2B(OH)_2Na$, which on acidification gave an acid, m. 70–3°, corresponding to $(p\text{-}ClC_6H_4)_2BOH.H_2O$. Cf. König and Scharrnbeck (*C.A.* 25, 927); Mel'nikov and Rokitskaya (*C.A.* 33, 4069[a]). G. M. Kosolapoff

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Organoboron compounds. VIII. Synthesis and properties of diarylborinic acids. B. M. Mikhailov and V. A. Vaver. Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci. 1956, 441-6 (Engl. translation).—See C.A. 50, 11064c.

B. M. R.

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Organoboron compounds. IX. Action of phosphorus pentachloride on esters of dialkylboric and alkylboric acids. Synthesis of dialkylboron chlorides and esters of alkylchloroboric acids. B. M. Mikhailov and T. A. Shchegoleva. *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.* 1956, 501-2 (Engl. translation).—See *C.A.* 50, 16664c. B. M. R.

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Effect of active nitrogen on organic materials. I. P. M. Aronovich and B. M. Mikhailov. II. P. M. Aronovich, N. K. Bel'skii and B. M. Mikhailov (*Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1956, 544—549, 696—701).—I. The activity of nitrogen with some org. materials, after activation in a tube discharge at 2100—2500 v, 140—180 ma. and 10—15 mm. pressure, duration 5—7 hr. and at [illegible] is discussed. Materials could be arranged in the following sequence of decreasing activity: [illegible] > benzene > *cyclo*hexanone > acetic acid > *n*-butyl ester of oleic acid > di-*n*-butyl ester of phthalic acid > oleic acid > stearic acid. Main reaction product in all cases was HCN. Reaction of active nitrogen on unsaturated and aromatic compounds resulted in formation of solid materials containing 18—26% of nitrogen; with *cyclo*hexanone, *cyclo*hexanone cyanohydrin was also formed, whilst oleic acid gave stearic acid.

II. The reactivity of active nitrogen with benzene (I) and with naphthalene (II) is similarly investigated. Three reaction products were separated from I, viz., phenyl *iso*nitrile, benzonitrile and pyridine (the latter was unexpected). Possibly, benzene molecules undergo deep cleavage through collision with N atoms, as a result of which [illegible] containing one or two carbon atoms are formed; these particles form pyridine through reactions with HCN. However, in the case of II, quinoline and *iso*quinoline were detected spectrographically but not pyridine.

A. L. B.

PM Frankel
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Organoboron compounds. X. Complex nature of salts of organoboron acids. B. M. Mikhailov, T. K. Kozminskaya, A. N. Blokhina, and T. A. Shchegoleva. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1956, 703-8 (English translation).—See *C.A.* 51, 1882h. B. M. R.

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Action of active nitrogen on organic compounds. II. B. M. Mikhailov. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (English translation). See C.A. 51, 1888

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No. 9

Polyene compounds. I. Synthesis of 1,5-aryl-substituted derivatives of 1,3,5-hexatriene. B. M. Mikhailov and G. S. Ter-Sarkisyan (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 1079-84.—To PhLi soln. from 16 g. PhBr and 1.42 g. Li in Et_2O was added over 45 min. an Et_2O soln. of 17.3 g. 3-methyl-6-phenyl-3,5-hexadien-2-one and the mixt. refluxed 3 hrs.; on the following day it was treated with H_2O, yielding from the org. layer 80% *3-methyl-2,6-diphenyl-3,5-hexadien-2-ol* (I), m. 08-85° (from EtOH). I dehydrates in part on distn. and b_3 220-3°, having the compn. after distn. 87.8% C and 7.6% H. Refluxing 5 g. I in 25 ml. Ac_2O and 3 g. AcONa 15 hrs. followed by quenching in H_2O-ice gave 4.5 g. yellow solid, m. 143-67°, which recrystd. from EtOH-C_6H_6 gave about 0.44 g. *4-methyl-1,5-diphenyl-1,3,5-hexatriene* (II), m. 202-3° (from AcOH), while the mother liquor treated with EtOH gave about 0.47 g. colorless *low-melting isomer* of II, m. 185-6.5° (from AcOH). The oil obtained similarly from 18.6 g. 3-methyl-6-phenyl-3,5-hexadien-2-one and PhLi was fractionated without isolation of the carbinols, yielding fractions, b_1 200-60°; the lower fraction yielded 1.9 g. 4-*methyl-1,5-diphenyl-1,3,5-hexatriene*, m. 92-2.5° (from MeOH), while the middle fraction gave a *low-melting isomer*, yellow liquid, b_2 170-3°, n_D^{20} 1.6243. The higher-melting isomer refluxed in Ac_2O-AcONa 15 hrs. gave II, m. 198-200°, and an isomer, m. 181-5°, which did not depress the m.p. of II. This isomerization took place also on heating the hydrocarbon 4 hrs. to 160-5°. 1-$C_{10}H_7Li$ (from 19 g. RBr) in Et_2O with 14.9 g. 3-methyl-6-phenyl-1,3-hexadien-2-one similarly gave 23.5 g. viscous oil which was freed of $C_{10}H_8$ by steam, and on extn. with EtOH gave a little perylene, m. 272-5°. The residual dark mass with dehydrated as

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Mikhailov, B. M. + Ter-Sarkisyan, G. S.

above with Ac_2O-AcONa yielding 12% *4-methyl-1-phenyl-6-(1-naphthyl)-1,3-5-hexatriene*, m. 230-1° (from C_6H_6-EtOH). Fluorenyllithium from 12.8 g. fluorene and PhLi was treated with 12 g. 3-methyl-6-phenyl-3,5-hexadien-2-one [illegible] which treated with [illegible] 6.05 g. difluorenyl[illegible], m. 148-50°. Ozonolysis of [illegible] contg. 93.99% C and 6.85% H, m. 148-50°. Ozonolysis of 4-methyl-6-phenyl-6-fluorenyl-3-hexen-2-one in $CHCl_3$ gave AcOH and *3-phenyl-3-fluorenylpropionaldehyde*, m. 225-7°; *2,4-dinitrophenylhydrazone*, m. 200°. Thus the addn. of PhLi and $C_{10}H_7Li$ occurs at the 1,2-positions of the triene, while fluorenyllithium adds in the 1,3-positions.

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Organoboron compounds. XII. Synthesis of arylboron dichlorides. B. M. Mikhailov and T. V. Kostroma (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 1144-6; cf. *C.A.* 51, 1882h, 2603h.—Addn. of 20.8 g. PCl_5 to 26.9 g. p-$ClC_6H_4B(OCH_2CHMe_2)_2$ (exothermic) followed by distn. gave 18.8 g. p-$ClC_6H_4BCl(OCH_2CHMe_2)$, b_{12} 121-3°, d_{20} 1.120. Similarly was prepd. 70% 1-$C_{10}H_7BCl(OCH_2CHMe_2)$, b_3 167.5-9°, d_{20} 1.091. Addn. of 83.4 g. PCl_5 to 46.8 g. $PhB(OCH_2CHMe_2)_2$, keeping the temp. 1 hr. at 70-80°, distg. RCl and $POCl_3$, and adding further 83.4 g. PCl_5 over 3.5 hrs. at 105-10° in a N stream, gave 60% $PhBCl_2$, b_{18} 73-5°. Similarly were prepd. 60.3% o-$MeC_6H_4BCl_2$, b_{20} 95-7°, and 62% p-$ClC_6H_4BCl_2$, b_{18} 106-7°.

G. M. Kosolapoff

MC

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Polyene compounds. II. Polyene compounds with heterocyclic substituents. B. M. Mikhailov and G. S. Ter-Sarkisyan (N. D. Zelinskii Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 1448-51; cf. *C.A.* 51, 5025*i*.—To PhLi (from 15.7 g. PhBr and 1.4 g. Li in 100 ml. Et_2O) was added 9.3 g. 2-methylpyridine and the cooled soln. of the RLi treated after 1 hr. with an unstated amt. of PhCH:CHCH:CMeAc (I), giving a ppt. which on the following day with H_2O yielded 17.4 g. *1-phenyl-4,5-dimethyl-6-(2-pyridyl)-1,3-hexadien-5-ol* (II), m. 86-7° (from EtOH); this treated with cooling with HCl in Et_2O and the ppt. neutralized with NH_4OH gave 100% *1-phenyl-4,5-dimethyl-6-(2-pyridyl)-1,3,5-hexatriene* (III), m. 98-9° (from EtOH, followed by chromatography on Al_2O_3). To the Li deriv. from 12.5 g. quinaldine and an equimolar amt. of PhLi in Et_2O was added with cooling an unstated amt. of I, yielding, as above, 59% *6-(2-quinolyl) analog* of II, m. 88-90° (from EtOH), which, treated as above in cooled Et_2O soln. with dry HCl, gave 85.6% *6-(2-quinolyl) analog* of III, m. 141-2° (from C_6H_6 and chromatography on Al_2O_3). 2-Methylpyridine treated with PhLi, as above, then with 11.9 g. PhCH:CHCHO, stirred after 1 hr. and treated with H_2O gave 45% *1-phenyl-4-(2-pyridyl)-1-buten-3-ol* (IV), m. 82-3° (cf. Späth, *et al.*, *C.A.* 35, 8901[5]), which, refluxed with AcOH in the presence of H_2SO_4 5 min., and neutralized, yielded 100% *1-phenyl-4-(2-pyridyl)-1,3-butadiene* (V), m. 123-4° (after chromatography on Al_2O_3). A similar reaction sequence with quinaldine instead of 2-methylpyridine gave 85.5% *4-(2-quinolyl) analog* of IV, m. 142° (from C_6H_6-EtOH), dehydrated as above to 83% *4-(2-quinolyl) analog* of V, m. 118-19°.

G. M. Kosolapoff

RM

MIKHAYLOV, B.M.

PM

Chem

Organoboron compounds. XIV. Reaction of organic bases with diphenylboron chloride. B. M. Mikhailov and N. S. Fedotov (N. D. Zelinskii Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 1511-13; cf. *C.A.* 50, 11964b; 51, 1874a, 4985h.—Addn. of 4.7 g. Et_2NH under N to 6.4 g. Ph_2BCl in Et_2O gave 3.53 g. $Et_2NH.HCl$ and 71.6% Ph_2BNEt_2, b_3 150-52°, d_{20} 0.0053, m. 36-7°, readily oxidized by air. Similarly, piperidine gave 63% $Ph_2BN(CH_2)_5$, b_5 200-2°, m. 65-6°. Passage of dry NH_3 into Ph_2BCl in Et_2O gave 60% $Ph_2B(NH_3)Cl$, softens 173-80°, does not completely m. 350°. Pyridine and Ph_2BCl in Et_2O gave 75.7% $Ph_2BCl.NC_5H_5$, m. 135-8°. Similarly were prepd. 74.0% p-$ClC_6H_4BPhCl.NC_5H_5$, m. 130-2°, and 75.3% $(1\text{-}C_{10}H_7)_2BCl.NC_5H_5$, m. 243-6°. O. M. Kosolapoff

MIKHAYLOV, B.M.; FEDOTOV, N.S.

Boron organic compounds. Part 6. Effect of phosphorus pentachloride on diarylboric acid esters. Synthesis of diarylborochlorides. Izv.AN SSSR.Otd.khim.nauk no.3:375-376 Mr '56. (MLRA 9:8)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii nauk SSSR.

(Phosphorus pentachloride) (Chlorides)

MIKHAYLOV B. M.

USSR/ Organic Chemistry - Synthetic organic chemistry E-2

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11792

Author : Mikhaylov B.M., Vavar V.A. (Communication 8)
Mikhaylov B.M., Shchegoleva T.A. (Communication 9)

Inst : Department of Chemical Schiences, Academy of Sciences USSR

Title : Organic Boron Compounds. Communication 8. Synthesis and Properties of Diaryl-Boric Acids. Communication 9. On Action of Phosphorus Pentachloride on Esters od Dialkyl-Boric and Alkyl-Boric Acids. Synthesis of Dialkyl Borochlorides and Esters of Alkyl-Chloroboric Acids.

Orig Pub : Izv. SSSR, Otd, khim. n, 1956, No4, 451-456; 508-509.

Abstract : Communication 8. Description of synthesis of $(\alpha-C_{10}H_7)_2BOH$ (I), $(p-BrC_6H_4)_2BOH$ (II) and $(p-ClC_6H_4)_2B(OH).H_2O$ (III) and study of the properties of the acids and their derivatives. $(\alpha-C_{10}H_7)_2BOC_4H_9$-iso (IV), $(p-BrC_6H_4)_2BOC_4H_9$-iso (V) and $(p-ClC_6H_4)_2BOC_4H_9$-iso (VI) were

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obtained from $(iso\text{-}C_4H_9O)_3B$ (VII) and the corresponding aryl-magnsium bromides. IV, V and VI are not hydrolyzed by water and acids and form with alkalies complexes of the type $[Ar_2B(OC_4H_9\text{-}iso)(OH)]$ Me (VIII). Salts of VII are con.'rted on heating in aqueous solutions to salts of diaryl-borenic acids $(Ar_2B(OH)_2)$Me (IX). Hydrolysis of IV, V and VI with aqueous solutions fo NH_4OH or $Ba(OH)_2$ results not in salts of di-aryl-boric acids but in complex salts IX (Me - NH_4; Ba/2). Acids I, II and III were obtained on acidification of the salts IX. As a result of treatment of I with excess $SOCl_2$ was isolated $((\alpha\text{-}C_{10}H_7)_2B)_2O$ (X). Results of the investigation show that literature data on II and III are erroneous. To 1 M ether-benzene solution of 0.5 mole α-$C_{10}H_7MgBr$ are added at -30° 0 225 mole VII in 50 ml ether. After stirring for 7 hours at -75°, treating the reaction products with 350 ml of 5% HCl, the ether-benzene solution is dried over Na_2SO_4.

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Residue after removal of solvents is diluted with isopentane, yield of IV 63%, MP 104-105° (from n-hexane). From filtrate, esterification of remaining iso-C_4H_9OH, were obtained 15% (α -$C_{10}H_7$)BOC_4H_9-iso, BP 166-168°/6 mm, d_4^{20} 0.9777. To a suspension of 10 g IV in 20 ml CH_3OH are added 15 ml of 30% NH_4OH. Obtained 97.5% [(α -$C_{10}H_7$)$_2$B(OH)$_2$] NH_4 (XI), MP 107-108° (from CH_3OH). Suspension of 4.94 g XI in 30 ml ether acidified with 5 ml HCl (1:1). From ether layer isolated 71.7% I, MP 114.5-115° (from petroleum ether). Solution of 2 g I in 5 ml $SOCl_2$ boiled 2 hours. After removal excess $SOCl_2$ obtained 98% X MP 190-192° (from benzene + petroleum ether). From 0.65 mole p-BrC_6H_4MgBr (1 M solution) and 0.25 mole VII, after stirring for 8 hours at -75°, treatment with 450 ml of 5% HCl and esterification, were obtained 39% V, BP 161-163°/1 mm, (in N_2 current) and 37% p-$BrC_6H_4B(OC_4H_9$-iso) BP 109-110°/1 mm, d_4^{20} 1.1583. 2.25 g V mixed by shaking with 5 ml 30%

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NH_4OH. Yield of $[(p\text{-}BrC_6H_4)_2B(OH)_2]NH_4$ (XII) 87.3%, MP 134-135° (from benzene). From solution of 1.23 g V in 3.65 ml 0.8 N KOH, was slowly driven off, at 60-70°, in a current of N_2, the water. Residue crystallized from mixture $C_6H_6 + CH_3OH$. Yield of $[(p\text{-}BrC_6H_4)_2B(OH)_2]K$ (XIII) 0.8 g. 1.65 g XII treated with dilute HCl, yield of II 86%, MP 90-91° (from petroleum ether). II was also obtained from XIII. After stirring for 8 hours at -75° 0.6 mole $p\text{-}ClC_6H_4MgCl$ (1 M solution) and 0.25 mole VII, treatment with 450 ml 5% HCl and esterification the reaction products are rapidly distilled in N_2 stream. As a result of fractionation isolated 40% VI, BP 134-135°/1 mm, d_4^{20} 1.1414, and 25% $p\text{-}ClC_6H_4B(OC_4H_9\text{-}iso)_2$, BP 93-95°/1 mm, d_4^{20} 1.0051. 1.73 g VI shaken with 15 ml saturated solution of $Ba(OH)_2$. Obtained 89.5% $[(p\text{-}ClC_6H_4)_2B(OH)_2]_2Ba$ (XIV). 2 g XIV treated with 10 ml HCl (1:4). Crystals of III

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washed with water and dried over $CaCl_2$. Yield 1.1 g, MP 76-78° (reprecipitated from alcohol with water). 2.85 g VI dissolved in 8.4 ml 1.09 N NaOH. Water slowly driven off in vacuum at 60-70°. Residue washed with C_6H_6. Obtained 2.2 g $((p\text{-}ClC_6H_4)_2B(OH)_2)Na$ (XV). From 0.3 g XV isolated on acidification 0.25 g III.

Communication 9. Study of interaction of PCl_5 with $(n\text{-}C_4H_9)_2BOC_4H_9\text{-}n$ (XVI) and with $(n\text{-}C_4H_9)(n\text{-}C_3H_7)BOC_4H_9\text{-}n$ (XVII). Reaction with XVI or XVII takes place with formation of $(n\text{-}C_4H_9)_2BCl$(XVIII) or, respectively, $(n\text{-}C_4H_9)(n\text{-}C_3H_7)BCl$ (XIX), C_4H_9Cl and $POCl_3$. It was also found that (n-C H)B(OC H -n) (XX) and (n-C H)B(OC H) (XXI) react readily with one equivalent of PCl_5, forming, respectively, $(n\text{-}C_3H_7)B(OC_4H_9\text{-}n)Cl$ (XXII) and $(n\text{-}C_4H_9)B(OC_4H_9\text{-}n)Cl$ (XXIII), C_4H_9Cl and $POCl_3$. To 16.8 g

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I were added, by increments, 17.6 g PCl_5. On completion of reaction C_4H_9Cl and $POCl_3$ removed in vacuum. Yield of XVIII 89%, BP 56-60°/ 12 mm. From 13.3 g XVII and 15 g PCl_5 obtained, as above, 50% XIX, BP 60-61°/28 mm, d_4^{20} 0.8503. Used in the reaction 20.2 g XXI and 19.6 g PCl_5. Obtained with 78% XXIII, BP 64-65°/10 mm, d_4^{20} 0.9025, 8.5 g C_4H_9Cl and 8.7 g $POCl_3$. To a solution of 160 g $(CH_3O)_3B$ in 400 ml ether added at -70° a solution of n-C_3H_7MgCl (from 36 g Mg, 116 g n-C_3H_7Cl and 600 ml ether). After treatment of reaction products with 10% solution of HCl and esterification with 400 ml n-C_4H_9OH obtained 44% XX, BP 82-83°/7 mm, d_4^{20} 0.8152. From 20.7 g XX and 21.5 g PCl_5 obtained 83% XXII, BP 60.6-61°/22 mm, d_4^{20} 0.8999.

Communication 7 see RZhKhim, 1957, 8097.

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Mikhaylov, B.M.

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Abs Jour : Ref Zhur - Khimiya, No. 8, 1957, 26676

Author : Aronovich, P.M.; Bel'skiy, N.K., Mihaylov, B.M.

Inst : Academy of Sciences of USSR.

Title : Action of Active Nitrogen on Organic Substances.

Orig Pub : Izv AN SSSR, Otd. khim. n., 1956, No. 5, 544 - 549.

Abstract : I. Cyclohexene, n-hexane, cyclohexane, C_6H_6, cyclohexanone (I), CH_3COOH, n-butyl esther of oleic acid, di-n-butyl ester of phthalic acid, oleic acid (II) and stearic acid (III) interact with active nitrogen at a speed decreasing in the above order and produce HCN and traces of dicyanogen. At the interaction with unsaturated and aromatic compounds, solid substances

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Abs Jour : Ref Zhur - Khimiya, No. 8, 1956, 26676.

are deposited on the walls of the vessel; these substances contain 16 to 26% of N and produce NH_3 at alkaline hydrolysis. Cyanohydrin is produced with I. The organic products of reactions of nitrogen with other substances are not identified. A small amount of III is produced from II. Nitrogen, dried and freed of O_2, is passed through a discharge tube at 2100 to 2500 v, 140 to 180 ma and under the pressure of 10 to 15 mm. The luminescent gas coming out of the tube passes through a test tube with the liquid under investigation or, in case of work with gaseous substances, is mixed with them in a tube of 2.5 cm in diameter or in a globe of 12 cm in diameter. The duration of the experiment is 5 to 7 hours daily, the total duration being

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10 to 50 hours. HCN in the amount of 1.6 mg per hour is forming from melted III at 70°, 7.7 mg of HCN per hour is forming from II at the same temperature, and 1.7 mg of it per hour is forming at about 20°.

II. The presence of pyridine (IV), phenylisonitrile (V), benzonitrile (VI) and, probably, dinitrile of terephthalic acid among the products of the reaction of active nitrogen with C_6H_6 was proved. At the action of IV on naphthalene (VII), quinoline and isoquinoline are produced together with other products. The absence of amines was proved in both cases. The following reaction mechanism was surmised:

$C_6H_6 + N \rightarrow C_6H_5 + NH$; $C_6H_5 + N \rightarrow C_5H_5 + CN$;

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MIKHAYLOV, B.M.; KOZMINSKAYA, T.K.; BLOKHINA, A.N.; SHCHEGOLEVA, T.A.

Boron organic compounds. Part 10. Complex nature of salts of boron-organic acids. Izv.AN SSSR Otd.khim.nauk no.6:692-695 Je '56.
(MIRA 9:9)

1.Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR.
(Boronium salts)

MIKHAYLOV, B.M.

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Complex lithium-aromatic compounds. N. G. Chernova and B. M. Mikhailov. J. Gen. Chem. U.S.S.R. 25, 2249-52(1955)(Engl. translation).—See C.A. 50, 9365f.
B. M. R.

Chem

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USSR/Organic Chemistry - Synthetic Organic Chemistry, E-2

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 938

Author: Mikhaylov, B. M., and Bronovitskaya, V. P.

Institution: None

Title: Synthesis of Thiazole Derivatives by the Use of Lithium-Organic Compounds

Original Periodical: Zh. obshch. khimii, 1956, Vol 26, No 1, 66-68

Abstract: The synthesis of 2,4-dimethyldiazolyl-5-lithium (I) is described together with its utilization in the synthesis of some 5-substituted 2,4-dimethyldiazoles. The carboxylation of I leads to the formation of 2,4-dimethylthiazole-5-carboxylic acid (II). The reaction of I with ethylene oxide yields 2,4-dimethyl-5-(β-ethoxy)-thiazole (III). Condensation of I with CH_2O and CH_3CHO yields 2,4-dimethyl-5-methoxy-(IV) and 2,4-dimethyl-5-α-ethoxythiazole (V), respectively. From V and CH_3I, 2,4,5-trimethylthiazole (VI) can easily be synthesized. All the reactions with lithium-organic compounds were carried under

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Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 938

Abstract: an atmosphere of N_2. To an ether solution of 0.516 gms C_6H_5Li add (<0°) an ether solution containing one gram of 2,4-dimethyl-5-bromothiazole (VII); after 15 minutes pour the mixture over dry ice, add ether and water, and acidify. II is obtained in yields of 73.5%, mp 230-231° (from water). To a solution of C_6H_5Li (from 24 gms C_6H_5Br and 2.1 gms Li in 90 ml absolute ether) add (<0°, an ether solution containing 20 gms VII, stir for 15 minutes, passing ethylene oxide through the solution, and hydrolyze. III is obtained in yields of 39.2%, bp 130-132°/6 mm. Similarly, if CH_2O vapor is passed through the mixture, IV is obtained (after 12 hours the solution is poured into dilute HCl and ice, neutralized with concentrated NH_4OH, and extracted with $CHCl_3$); the yield is 64%, bp 123-125°/4 mm, mp 43-45°, picrate - mp 106-107° (from alcohol), hydrochloride - mp 151-153° (from absolute alcohol). To I prepared from 20 gms VII add 9.2 gms CH_3CHO, mix at 20°, pour into dilute HCl and ice; V separates as an oil, as described above; yield 41.5%. The product decomposes on standing. From I (30 gms VII) and 66 gms CH_3I, VI is obtained in yields of 68.6%, bp 48-50°/14 mm; picrate, mp 135-136.5° (from alcohol).

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MIKHAYLOV, B.M.; PLATOVA, I.K.

Mannich reaction in the thiazole series. Zhur.ob.khim. 26 no.2: 491-493 F '56. (MLRA 9:8)
(Mannich reaction) (Thiazole)

Structure and chemical transformations of alkali metal organic compounds of anils. II. Transformations of disodium and dilithium compounds of benzophenone phenylimine under the action of alkyl halides. B. M. Mikhailov and K. N. Kurdyumova. *Zhur. Obshchei Khim.* 26, 733-9 (1956); cf. *C.A.* 50, 6891h.—The alkali metal derivs. of $Ph_2C:NPh$ react with org. halides in a series of transformations. The 1st step is the exchange of an ionized metal ion for H yielding a monometallic deriv. which then partly passes into phenylbenzhydrylamine and partly exchanges the metal for the org. radical of the halide, with breakage of the C-N bond forming 1,1-diphenylethylenic hydrocarbons, $PhNH_2$, and analogs of tetraphenylbutane (cf. Schlenk and Bergmann, *C.A.* 22, 4499). All reactions below were run under N_2. Benzophenone anil (20 g.) in 200 ml. Et_2O was shaken 60-70 hrs. with 0.18 mole Na or 0.25 mole Li with glass beads to form the metallic deriv. The di-Na deriv. suspension treated with MeI (11.4 g.) in Et_2O gave much heat, gaseous products, and formed a brown soln.; the org. layer gave 2 g. oily material which with 100 g. hot 20% HCl (0.5 hr.) gave the phenylbenzhydrylamine HCl salt, m. 188-90°; free amine, b_4 180-2°, m. 56-7°, obtained in 25% yield. The residual soln. gave 48.2% $PhNH_2$, 18.6% $Ph_2C:CH_2$, and 8% 2,2,3,3-tetraphenylbutane; the gaseous products were 32% CH_4, 62.5% C_2H_4, 2.8% C_2H_6, and 2.5% [illegible], a total of [illegible] ml. of gases being collected. PhLi from 31.4 g. PhBr and 2.8 g. Li in Et_2O were treated with 10.3 g. acetophenone anil and refluxed 6 hrs.; after aq. treatment there formed 55% *1,1-diphenylethylphenylamine*, b_4 195-7°, m. 50-3° (*HCl salt* (I), m. 190-1°). This (10 g.) added to

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Mikhailov, B. M. and Kordyumova, K. N.

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PhLi from 9.4 g. PhBr in Et_2O gave a red soln. of the Li deriv., which treated with 5.2 g. MeI with cooling and kept 2 hrs. gave after aq. treatment 28% I, 54.4% $Ph_2C:CH_2$, 1.1% 2,2,3,3-tetraphenylbutane, and 43.8% PhNHMe. The di-Li deriv. of benzophenone anil with MeCl gave 37.5% phenylbenzhydrylamine, 52.6% $PhNH_2$, 20.4% $Ph_2C:CH_2$, and 8% 2,2,3,3-tetraphenylbutane; with MeI these amounts were 18.4, 60.9, 28, and 9.1%, resp.; with EtI these were 22.8, 60.9, — (45.3% $Ph_2C:CHMe$), —. The di-Na deriv. with EtI gave: 32.2, 50.9, — (32% $Ph_2C:CHMe$), —; with PrI this gave 35.3, 54.1, — (35.3% $Ph_2C:CHEt$, b_8 120-3°, d_{16} 1.031, n_D^{16} 1.160), —. The di-Li deriv. with $PhCH_2Cl$ gave, resp.: 18.2, 59.5, — (55.7% $Ph_2C:CHPh$), —. G. M. Kosolapoff

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MIKHAYLOV, B. M.

2

Structure and chemical transformations of alkali metal organic compounds of anils. II. Transformations of disodium and dilithium compounds of benzophenone phenylimine under the action of alkyl halides. B. M. Mikhailov and K. N. Kurdyumova. J. Gen. Chem. U.S.S.R. 26, 899-903(1956)(English translation).—See C.A. 50, 14656i.
B. M. R.

APPROVED FOR RELEASE: 07/12/2001 CIA-RDP86-00513R001034010002-0"

~~MIKHAYLOV B.M.~~ Mikhaylov, B. M.

Some 2-chloroethyl and ethylenimino derivatives of pyridine. B. M. Mikhailov and T. K. Kozminskaya. Zhur. Obshchei Khim. 26, 2042-6 (1956).—The following substances were prepd. for cancer studies, as analogs of mustard gases. Reduction of 2,6-dimethyl-3,5-dicarbethoxypyridine with LiAlH$_4$ (cf. Bohlmann and Bohlmann, C.A. 49, 2434d) with the reaction mixt. being heated 3 hrs. and [illegible] overnight before hydrolysis, gave 70% 2,6-dimethyl-3,5-bis(hydroxymethyl)pyridine, m. 131-3°, which (1.5 g.) and 6 ml. SOCl$_2$ refluxed 1.5 hrs., freed of excess SOCl$_2$, and treated with a little H$_2$O gave 86.2% 2,6-dimethyl-3,5-bis(chloromethyl)pyridine (I), m. 105-7° (crude), m. 107-8.5° (from [illegible] ether). This (2 g.) and HN(CH$_2$CH$_2$Cl)$_2$ (from [illegible] salt) refluxed in C$_6$H$_6$-CHCl$_3$ 60 hrs. gave after [illegible] pptd. amine-HCl, 22% 2,6-dimethyl-3,5-bis[bis(2-chloroethyl)aminomethyl]pyridine, m. 99-100° (from Et$_2$O). Ethylenimine (5.1 ml.) and 3 g. NaNH$_2$ stirred 1 hr. at 30° in Et$_2$O and 4.75 g. I added at −10° gave 91% 2,6-dimethyl-3,5-bis(ethyleniminomethyl)pyridine, m. 71-2° (from Et$_2$O). Treatment of isonicotinic acid with SOCl$_2$ and the acid chloride refluxed 8 hrs. with HN(CH$_2$CH$_2$Cl)$_2$ in C$_6$H$_6$-CHCl$_3$ gave 90% isonicotinic bis(2-chloroethyl)amide, m. 95-7° (from EtOH). Similarly nicotinic acid gave 84% of the corresponding bis(2-chloroethyl)amide, m. 53-4° (from C$_6$H$_6$-petr. ether). Heating 20 g. 2,6-dimethyl-3,5-dicarbethoxypyridine with 20 ml. H$_2$NCH$_2$CH$_2$OH and 2-3 drops pyridine 8 hrs. at 180° gave 86% 2,6-dimethyl-3,5-pyridinedicarboxylic acid di-2-hydroxyethylamide, m. 189-90° (from EtOH), which treated with SOCl$_2$ in CHCl$_3$ with cooling gave after 24 hrs. 86% 2,6-dimethyl-3,5-pyridinedicarboxylic acid di-2-chloroethylamide-HCl, m. 227-9°; the free amide, m. 178-9° (from EtOH).

G. M. Kosolapoff

MIKHAYLOV, B. M.

Synthesis of β-chloroethylamine derivatives of thiazole. B. M. Mikhailov, V. P. Bronovitskaya, and I. K. Platova. Zhur. Obshchei Khim. 26, [illegible](1956).—The following derivs. were prepd. for evaluation as cancerolytic agents. Heating of [illegible] g. 2-bromothiazole with 41.8 g. $NH(CH_2CH_2OH)_2$ in 50 ml. pyridine 10 hrs. at 120-30°, concn. in vacuo, diln. of the residue with H_2O and addn. of K_2CO_3 and extn. with Et_2O gave 10.2 g. 2-di(2-hydroxyethyl)aminothiazole, b_4 104-6°; HCl salt, m. 199.5-90°. This (7.5 g.) added slowly in 15 ml. $CHCl_3$ to 6 ml. $SOCl_2$ in $CHCl_3$ at −10°, stirred 0.5 hr., kept overnight at room temp., refluxed [illegible] hrs., concd., and treated with C in EtOH gave [illegible] 2-di(2-chloroethyl)aminothiazole-HCl, m. [illegible]. Similarly 4-chloromethylthiazole and $NH(CH_2CH_2OH)_2$ in EtOH after 20 hrs. on a steam bath gave 31% 4-di(2-hydroxyethyl)aminomethylthiazole, b_4 195-7° (picrate, m. 102-4°), which this with $SOCl_2$ as above gave 22% 4-di(2-chloroethyl)aminomethylthiazole-HCl, decomp. 207-8°. Similar treatment of 2-methyl-4-chloromethylthiazole gave 48.6% 2-methyl-4-di(2-hydroxyethyl)aminomethylthiazole, b_4 192-4°, which gave 80.5% 2-methyl-4-di(2-chloroethyl)aminomethylthiazole-2HCl, m. 223-4.5°. Treatment of 2,4-dimethyl-5-(hydroxymethyl)thiazole in $CHCl_3$ at −5° with $SOCl_2$ as above gave 60% 2,4-dimethyl-5-chloromethylthiazole, m. 01-8° (from dry EtOH), which gave 63.7% 2,4-dimethyl-5-di(2-hydroxyethyl)aminomethylthiazole, b_4 205-7°, which gave 44% 2,4-dimethyl-5-di(2-chloroethyl)aminomethylthiazole-2HCl, m. 104-6°. Treatment of 4-methyl-5(2-hydroxyethyl)thiazole with $SOCl_2$ in $CHCl_3$ at −5° similarly gave 60% 4-methyl-5-(2-chloroethyl)thiazole, b_4 97-8°, which gave 87.6% 4-methyl-5-di(2-hydroxyethyl)aminoethylthiazole, b_4 200-8°, n_D^{20} 1.5618 (picrate, m. 132-3°), which in $CHCl_3$ treated with dry HCl, then with $SOCl_2$ gave after heating 2 hrs. 48.7% 4-methyl-5-di(2-chloroethyl)aminoethylthiazole-2HCl, m. 178-80°. G. M. Kosolapoff

MIKHAYLOV, B.M.

4E4j

Organoboron compounds. synthesis of trialkyl compounds of boron from the esters of dibutylboric acid. B. M. Mikhailov and T. A. Shchegoleva. *Proc. Acad. Sci. U.S.S.R., Sect. Chem.* 108, 281-3(1956)(English translation).—See C.A. 51, 1026c. B. M. R.

4E3d

MIKHAYLOV, B.M.

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Organoboron compounds. Synthesis of trialkyl compounds of boron from the esters of dibutylboric acid. B. M. Mikhailov and T. A. Shchegoleva. *Doklady Akad. Nauk S.S.S.R.* 109, 481-3(1956).—To Et_2O soln. of BuLi from 3.5 g. Li and 27.4 g. BuCl in 180 ml. Et_2O was added at −70° 27.8 g. Bu_2BOBu over 40 min.; after stirring 3 hrs. the mixt. was left overnight, after which it was acid. with dry HCl, filtered of Li halides and distd.; the fraction, b_{12} 114-19°, was shaken with 10% NaOH, the 2 layers were sepd. and the org. layer was freed of BuOH and H_2O by distn.; the residue was dild. with 20 ml. H_2O, and the org. layer which sepd. was azeotropically dried with C_6H_6 and distd., yielding 38% Bu_3B, b_{12} 109-10°. Similarly, PrLi from 4.55 g. Li with 60 g. Bu_2BOBu gave 60% Bu_2BPr, b_{12} 75-80°, and 3.5 g. unreacted ester. Pure Bu_2BPr b_{12} 77-9°, d_{20} 0.7484. When this was fractionated slowly through a 20-plate column, there was obtained an appreciable amt. of Pr_3B, b_{12} 60.5-4° and Bu_3B, b_{12} 98-8°. Reaction of EtLi from 4.45 g. Li with 44.8 g. Bu_2OBu at −25° similarly gave a series of fractions from which was isolated 26% Bu_2BEt, b_{12} 67-9°. The analysis of the B compds. was simplified (cf. Snyder, *et al.*, *C.A.* 32, 1040[4]) by the following technique. The sample (0.1-0.2 g.) is treated with 1 ml. 6N NaOH and 5 ml. 30% H_2O_2; after the vigorous reaction subsides, there is added 2 ml. 6N NaOH and 3 ml. 30% H_2O_2 and the mixt. refluxed 20 min., treated with 20 ml. N HCl, and refluxed again 20 min.; on cooling the excess HCl is neutralized by N NaOH with methyl orange indicator, treated with mannitol and titrated with 0.1N NaOH with phenolphthalein indicator. G. M. Kosolapoff

MIKHAYLOV, B.M.; VAVER, V.A.

[redacted]

Organoboron compounds. Thepreparation of complex compounds of unsymmetric boron triaryls. Dokl. AN SSSR 109 no.1:94-97 Jl-Ag '56. (MLRA 9:10)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii nauk SSSR. Predstavleno akademikom B.A. Kazanskim.

(Boron organic compounds)

1

Organoboron compounds. Synthesis of complex compounds of unsymmetric boronitriaryls. B. M. Mikhailov and V. A. Vaver. Proc. Acad. Sci. U.S.S.R., Sect. Chem. 109, 511-14(1956)(English translation).—See C.A. 51, 1874e. B. M. R.

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4E4j

4E2c (j)

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MIKHAYLOV, B.M.

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4E4j

4E3d

Organoboron compounds. XV. Organoboron compounds with an asymmetric boron atom. B. M. Mikhailov, T. V. Kostroma, and N. S. Fedotov (N. D. Zelinskii Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1957, 589-97; cf. *C.A.* 50, 11954b; 51, 1832h, 8075d.—Addn. of 19.0 g. $PhB(OCH_2CHMe_2)Cl$ in Et_2O of o-MeC_6H_4MgBr from 20.5 g. RBr gave after removal of Et_2O, addn. of isopentane, filtration, and distn. 62.1% o-$MeC_6H_4BPhOCH_2CHMe_2$ (I), b_{14} 155-6°, d_{20} 0.9714, n_D^{20} 1.5370; similarly, p-BrC_6H_4MgBr gave 34.7% p-BrC_6H_4-(o-MeC_6H_4)$BOCH_2CHMe_2$, b.p. unstated, 1.1759, 1.5016. Similarly, p-ClC_6H_4MgBr gave 44.4% p-$ClC_6H_4BPhOCH_2CHMe_2$ (II), b_2 137-9°, 1.0351, 1.5433. I (20 g.) treated with 23.5 g. PCl_5 gave 67.2% o-MeC_6H_4BPhCl (IIa), b_3 143-6°, d_{20} 1.080; this treated with H_2O [illegible] with isopentane, and thoroughly dried *in vacuo* gave 84.2% o-$MeC_6H_4B(OH)Ph.H_2O$, a liquid, which on standing gradually formed the anhydride of [illegible]boronic acid (III). Similarly, II gave 47% p-ClC_6H_4BPhCl, b_2 135-40°, d_{20} 1.145, which with H_2O gave 78% p-$ClC_6H_4B(OH)Ph.H_2O$, liquid, gradually changing to III on standing. Ph_2BCl and o-MeC_6H_4MgBr gave in 7 hrs. 41% o-$MeC_6H_4BPh_2$, b_2 167-9°, which oxidizes in air. Similarly, IIa and p-MeC_6H_4MgBr gave (o-MeC_6H_4)$BPhC_6H_4Me$-p (IV), 45.4%, b_2 168-70°. Similarly was prepd. 40% o-MeC_6H_4B(C_6H_4Cl-p)Ph (V), b_2 163-7°, slowly solidifying on standing. Refluxing 10 g. Ph_2BCl with o-MeC_6H_4Li from 11 g. RBr 8 hrs. in Et_2O gave 2.8 g. (o-MeC_6H_4)$_2BPh_2Li$ and 4.7 g. o-$MeC_6H_4BPh_2$, b_2 177-80°. The latter with 1-$C_{10}H_7Li$ in Et_2O gave 40% [1-$C_{10}H_7BPh_2C_6H_4Me$-o]Li, a solid, isolated as an adduct with 2 mols. Et_2O. This with satd. KCl gave [1-$C_{10}H_7BPh_2C_6H_4Me$-o]K, colorless solid. IV similarly gave [illegible] with KCl [illegible] V and 1-$C_{10}H_7Li$ similarly gave [illegible] (p-ClC_6H_4)$BPhC_{10}H_7$-1]Li [illegible] solid, yielding with KCl the K salt [illegible]

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APPROVED FOR RELEASE: 07/12/2001 CIA-RDP86-00513R001034010002-0"

Mikhailov, B.M.; Kostroma, T.V.; Fedotov, N.S.

...cryst. powder. XVI. Esters of aryl(alkylamino)boric acids. B. M. Mikhailov and T. V. Kostroma (N. D. Zelinskii Inst. Org. Chem., Moscow). *Ibid.* 646-8. —PhB(OCH$_2$CHMe$_2$)Cl (8 g.) in Et$_2$O treated at −30° with 5.0 g. Et$_2$NH and filtered after 1 hr. at room temp. gave from the filtrate 67% *iso-BuOB(NEt$_2$)Ph*, b$_2$ 92-4°, n_D^{20} 1.4822, d_{20} 0.8931. Similarly, Me$_2$NH gave 60.4% *iso-BuOB(NMe$_2$)Ph*, b$_2$ 68-70°. Similarly were prepd.: 47.2% *iso-BuOB(C$_{10}$H$_7$-1)NEt$_2$*, b$_2$ 127-8°, 1.5378, 0.9502; 67% *iso-BuOB(C$_6$H$_4$Me-o)NEt$_2$*, b$_2$ 122.5-3°, 1.4808, 0.8877; 68% *iso-BuOBPhNHEt*, b$_2$ 66-7°, 1.4831, 0.9057. All operations were performed under dry N.

G. M. Kosolapoff

1-4E4j

1-4E3d

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Mikhaylov, B. M.

Distr: 4E4j/4E3d/4E2c(j)

Organoboron compounds. XVII. Reaction of amine complexes of esters of diarylboric acid and organolithium compounds. Synthesis of unsymmetric triarylborons. Mikhailov and V. A. Vaver (N. D. Zelinskii Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1957, 812-17; cf. *C.A.* 50, 11904c; 51, 15440b. —To the complex from 10.01 g. iso-AmOBPh$_2$ and 3.14 g. pyridine in 10 ml. Et_2O was added 8.75 g. 1-$C_{10}H_7Li.Et_2O$ in 50 ml. Et_2O; after refluxing 4 hrs. the mixt. was washed with H_2O and yielded on evapn. and diln. with MeOH 67.5% *1-$C_{10}H_7BPh_2.C_5H_5N$*, decomp. 175-80°. Similarly, iso-BuOBPh$_2$ and *p*-MeC_6H_4Li gave 77% *p-$MeC_6H_4BPh_2.C_5H_5N$* (I), m. 166-8° (dil. MeOH). Also prepd. were 87% *o-$MeC_6H_4BPh_2.C_5H_5N$*, m. 177-9° (aq. Me_2CO); 91% *(1-$C_{10}H_7)_2BPh.C_5H_5N$*, decomp. 215-17°; 77% *o-(1-$C_{10}H_7)_2BC_6H_4Me.C_5H_5N$*, m. 203-5°; 72% *o-(p-$BrC_6H_4)_2BC_6H_4Me.C_5H_5N$*, m.p. not given. To 8.04 g. iso-BuOBPh$_2$.NH$_3$ was added 0.03 mole *p*-MeC_6H_4Li and after 4 hrs. refluxing in Et_2O the mixt. gave 53% *p-$MeC_6H_4BPh_2.NH_3$*, decomp. 189-91° (C_6H_6); similarly was prepd. 42.5% *(p-$ClC_6H_4)_2BPh.NH_3$*, m. 213-15° (EtOH). I with 30% H_2SO_4 in Et_2O under N gave 49% *p-$MeC_6H_4BPh_2$*, b_2 170-3°, which solidifies on chilling. The above listed complexes can also be converted to the free R_3B by treatment with dry HCl in Et_2O; thus was prepd. *p*-$MeC_6H_4BPh_2$ from the corresponding adduct with NH_3. Pyrolysis of $(1-C_{10}H_7)_2BPh.C_5H_5N$ in a sausage flask at 175-85° gave 87.5% C_5H_5N and 45% *(1-$C_{10}H_7)_2BPh$*, m. 146-8°, b_2 230-40°. Similarly was obtained *(1-$C_{10}H_7)_2BC_6H_4Me$-o*, $b_{0.08}$ 197-9°. $Ph_3B.NH_3$ in Et_2O treated with dry HCl gave 62.5% Ph_3B; the pyridine complexes above can also be decompd. to R_3B by picric acid in C_6H_6.

G. M. Kosolapoff

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MIKHAYLOV, B.M.

Distr: 4E4j/4E3d/4E2c(j)

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Organoboron compounds. XVIII. New method of synthesis of diarylborinic acids. B. M. Mikhailov and V. A. Vaver (N. D. Zelinskii Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1957, 989-91; cf. *C.A.* 51, 3487c; 52, 3667h.—To 0.2 mole PhMgBr was added with cooling 9 g. (iso-$BuOBO)_3$ in C_6H_6, the mixt. refluxed 1 hr. and treated with 200 ml. 3.5% HCl, and the org. layer, sepd. rapidly and evapd. rapidly *in vacuo* with min. heating, yielding on addn. of Et_2O-hexane to the residue 8.3 g. *phenylboronic anhydride*, m. 190-3°, while the mother liquor after evapn. and addn. of isopentane gave 51.0% $(Ph_2B)_2O$, m. 130-1°. The combined distillates gave iso-BuOH and some H_3BO_3. PhMgBr treated as above with $(C_5H_{11}OBO)_3$ and the crude product treated with $HOCH_2CH_2NH_2$ gave 62% $Ph_2BOCH_2CH_2NH_2$, m. 190-1° (EtOH). (iso-$BuOBO)_3$ with 1-$C_{10}H_7MgBr$ gave similarly after treatment with 3.5% HCl 76.6% $(1\text{-}C_{10}H_7)_2BOH$, m. 114-15°. Similar reaction of p-MeC_6H_4MgBr and treatment of the crude product with $HOCH_2CH_2NH_2$ gave 41% $(p\text{-}MeC_6H_4)_2BOCH_2CH_2NH_2$, m. 174.5-76° (EtOH), along with 21.2% $p\text{-}MeC_6H_4B(OCH_2CHMe_2)_2$, $b_{1.5}$ 127-8°, d_{20} 0.9100, n_D^{20} 1.4761. The use of 0.2 mole o-MeC_6H_4MgBr and 0.03 mole (iso-$BuOBO)_3$ gave after esterification of crude products with iso-BuOH 21% $o\text{-}MeC_6H_4B(OCH_2CHMe_2)_2$, b_2 111-15°, and 42% $(o\text{-}MeC_6H_4)_2BOCH_2CHMe_2$, $b_{1.5}$ 161-3°, 0.9701, 1.5432. The latter ester is slowly oxidized by contact with air.

G. M. Kosolapoff

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Mikhaylov, B.M.

Distr: 4E4j/4E2c(j)/
4E3d

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Organoboron compounds. XIX. Synthesis of alkyl-
boron dichlorides. B. M. Mikhailov and T. A. Shche-
golova (N. D. Zelinskii Inst. Org. Chem., Moscow).
[illegible] Khim. Nauk 1957,
1080-4; cf. C.A. 50, 10642; 52, 4532. To 180 g. B(OBu)$_3$
in 400 ml. Et_2O was added at −75° over 3 hrs. EtMgBr
from 80 g. Mg and on the following day (all operations
under N) the mixt. treated with dil. HCl, and the org. layer
freed of Et_2O, and slowly distd. with BuOH until the temp.
of the distillate reached 115° yielding 53% *EtB(OBu)$_2$*,
b$_7$ 70–1°, d$_{20}$ 0.8224. Similarly was prepd. 50% *iso-Pr-
B(OBu)$_2$*, b$_7$ 78–8.5°, d$_{20}$ 0.8187. Slow distn. of EtB-
(OBu)$_2$ and hexyl alc. gave 83.5% *EtB(OC$_6$H$_{13}$)$_2$*, b$_4$ 130–1°,
d$_{20}$ 0.8302; similarly was prepd. 80% *PrB(OC$_6$H$_{13}$)$_2$*, b$_7$
130–1°, d$_{20}$ 0.8283, and 72% *iso-PrB(OC$_6$H$_{13}$)$_2$*, b$_4$ 125–6°, 8
d$_{20}$ 0.8258. To 28.5 g. EtB(OBu)$_2$ was added over 1 hr.
31.8 g. PCl_5 yielding on distn. 78% *EtB(OBu)Cl*, b$_{50}$ 49– 2 May
52°, d$_{20}$ 0.9030, BuCl, and $POCl_3$. Similar addn. to 32.2 g.
EtB(OC$_6$H$_{13}$)$_2$ of 55 g. PCl_5 and refluxing 0.5 hr. gave 50%
EtBCl$_2$, b. 49–51°, which ignites in air and is easily hy-
drolyzed; the same formed in 40% yield from 17.5 g. Et- 2
B(OBu)Cl and [illegible] g. PCl_5. EtB(OC$_6$H$_{13}$)$_2$ (56 g.) with
[illegible] EtBCl$_2$, 19.5 g. EtB(OC$_6$H$_{13}$)Cl, 1
46.5 g. PCl_5 gave 8.4 g. EtBCl$_2$, 19.5 g. EtB(OC$_6$H$_{13}$)Cl,
b$_4$ 63–5°, and 21% EtB(OC$_6$H$_{13}$)$_2$. PrB(OC$_6$H$_{13}$)$_2$ (31.35 g.)
with 31.5 g. PCl_5 gave 73.5% *PrBCl$_2$*, b. 75–6°, which also
ignites in air. Similarly, 28.5 g. iso-PrB(OC$_6$H$_{13}$)$_2$ and
46.7 g. PCl_5 gave 70% *iso-PrBCl$_2$*, b. 70.5–73°, which 1
ignites in air. XX. *N*-Substituted phenyldiaminoborons and
B-phenylborazoles. B. M. Mikhailov and P. M. Aronovich. 2
Ibid. 1123–8; cf. *C.A.* 51, [illegible].—To 43.4 g. $EtNH_2$ in
C_6H_6 was added at −80° 31.8 g. $PhBCl_2$ in 80 ml. C_6H_6
and after warming to room temp. 2 hrs. the mixt. filtered
from $EtNH_2$.HCl and evapd. yielding 3.5 g. *B,B,B-triphenyl-
N,N,N-triethylborazole*, m. 200–3°; the mother liquor from
this gave *PhB(NHEt)$_2$* (I), b$_4$ 97–8°, d$_{20}$ 0.924, n_D^{20} 1.5120;

B. M. MIKHAILOV + T. A. SHCHEGOLEVA

The latter is readily attacked by H_2O and atm. O. The residue after the distn. gave more tri(phenyltriethylborazole (in a total yield of 21%; the pure substance, m. 205-7° (C_6H_6-petr. ether)); the borazole is stable in air and is slowly attacked by hot alk. H_2O. Heating I to 210° 2 hrs. gave 17.8% triphenyltriethylborazole. Addn. of 12.7 g. $PhBCl_2$ to 29.6 ml. $PhNH_2$ in C_6H_6 as above gave 84.7% *PhB-(NHPh)₂*, m. 83.5-5.5° (hexane-isopentane), which is rapidly hydrolyzed by H_2O. Heating this to 270° gave $PhNH_2$ and 31.7% *hexaphenylborazole*, m. above 300° (C_6H_6). $PhBCl_2$ and Et_2NH similarly gave 14.1% *PhB-(NEt₂)₂*, $b_{0.5}$ 70-2°. All work was done under N. XXI. New methods of synthesis of borazole derivatives. B. M. Mikhailov and T. V. Kostroma. *Ibid.* 1126-7.—*p*-$MeC_6H_4B(OCH_2CHMe_2)_2$ (92 g.) with 48.6 g. PCl_5 gave 87.8 % *p*-$MeC_6H_4BCl(OCH_2CHMe_2)$, b_4 113-15°, n_D^{20} 1.5017, d_{20} 0.9919. (iso-BuO)BPhCl (17.8 g.) treated with NH_3 in Et_2O gave after sepn. of NH_4Cl and evapn. 3.85 g. *B,B,B-triphenylborazole*, m. 180-2°, and 79% *PhB(OBu-iso)₂*, b_5 124-6°. Pure *triphenylborazole* m. 181-2.5° (C_6H_6-isopentane); $PhBCl_2$ in C_6H_6 with NH_3 gave 96% above triphenylborazole, m. 180-2°. Similarly were prepd. from the appropriate chloro esters 83% *B,B,B-tri(p-tolyl)-borazole*, m. 189-90°, and 84.9% *tri(1-naphthyl)borazole*, m. 186-7°, while the use of appropriate amines gave 72.0% *B,B,B-triphenyl-N,N,N-triethylborazole*, m. 205-6°, and 46.6% *B,B,B-tri(1-naphthyl)-N,N,N-triethylborazole*, m. 268-71°.

O. M. Kosolapoff

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Distr: 4E4j/4E2c(j)/
4E3d

Condensation of benzaldehyde acetal with vinyl ethyl ether. B. M. Mikhailov and L. S. Povarov (N. D. Zelinskii Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1957, 1239-44; cf. U.S. 2,165,962, *C.A.* 33, 8210[5].—To 140 g. $PhCH(OEt)_2$ was added 0.28 g. $Et_2O\text{-}BF_3$ and the soln. treated at 40° with 60 g. $EtOCH{:}CH_2$; after stirring 15 min., the mixt. was neutralized with dry Na_2CO_3, stirred 3 hrs., filtered, and distd. yielding 71.9% *(1,3,3-triethoxypropyl)benzene* (I), b_2 130-1°, b_1 97-8°, d_{20} 0.9642, n^{20}_D 1.4724, and 4% *(1,3,5,5-tetraethoxyamyl)benzene* (II), b_1 157-9°, 0.9659, 1.4703. I with more $EtOCH{:}CH_2$ as above gave 50% II and much higher-boiling material which yielded *(1,3,5,7,7-pentaethoxyheptyl)benzene*, b_1 156-8°, 0.9689, 1.4682, and *(1,3,5,7,9,9-hexaethoxynonyl)benzene*, b_1 180-2°, 0.9683, 1.4670. Boiling I with 2% HCl gave a distillate of EtOH and 88% *(1-ethoxy-3-oxopropyl)benzene*, b_1 80-1°, 1.0210, 1.5087. Similar hydrolysis of II gave 75% *(1,3-diethoxy-5-oxoamyl)benzene*, b_1 111-12°, 1.0060, 1.4960. G. M. Kosolapoff

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MIKHAYLOV, B.M.; KOSTROMA, T.V.

Boron organic compounds. Report No.16: Arylalkylaminoboric acid esters. Izv. AN SSSR. Otd. khim. nauk no.5:646-648 My '57. (MIRA 10:8)

1. Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR.

(Boric acid)

MIKHAYLOV, B.M.; VAVER, V.A.

Boron organic compounds. Report No.18: A new method for the synthesis of diarylboric acids. Izv. AN SSSR. Otd. khim. nauk no.8:989-991 Ag '57. (MIRA 11:2)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR. (Boric acid)

MIKHAYLOV, B.M.; ARONOVICH, P.M.

Boron organic compounds. Report No.20: N-substituted of phenyldiamino-boron and B-phenylborazoles. Izv. AN SSSR. Otd. khim. nauk no.9:1123-1125 S '57. (MIRA 10:12)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.
(Borazole) (Boron compounds)

MIKHAYLOV, B.M.; KOSTROMA, T.V.

Boron organic compounds. Report No.21: New methods for the synthesis of borazole derivatives. Izv. AN SSSR. Otd. khim. nauk no.9:1125-1127 S '57. (MIRA 10:12)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR. (Borazole)

Bromination of thiazole derivatives with *N*-bromosuccinimide. B. M. Mikhailov and V. P. Bronovitskaya. *Zhur. Obshchei Khim.* 27, 726–31(1957).—Heating 19 g. thiazole, 21 g. $(CH_2CO)_2NBr$ (I), and 35 ml. dry CCl_4 to 67° resulted in a vigorous reaction; after 45 min. of heating, the mixt. was cooled, filtered, and washed with dil. NaOH, yielding on distn. 12.5% *2-bromothiazole*, b_{15} 70–5°. This (1.64 g.) treated with BuLi, from 1.65 g. BuCl and 0.25 g. Li, in Et_2O at −40°, shaken under N 15 min. and treated with 1.1 g. BzH and shaken 45 min. gave after treatment with dil. HCl *2-thiazolylphenylcarbinol*, m. 104–7°. Similarly, 18 g. 4-methylthiazole, 32 g. I, and 50 ml. CCl_4 heated as above 30 min. gave 26% *4-methyl-2-bromothiazole*, b_{20} 79–81°, n^{20}_{D} 1.5776, d^{20}_{20} 1.7045; *HBr salt*, m. 169–70°. Refluxing 5 g. 4-chloromethylthiazole with 7.5 g. KOAc and 10 ml. AcOH 2 hrs. gave on diln. with H_2O 79% *4-thiazolylmethyl acetate*, b_{15} 117–19° (*picrate*, m. 129–31°), which kept overnight in 12% alc. KOH in the cold gave 77.5% *4-hydroxymethylthiazole*, b_{15} 123–5° (*picrate*, m. 158–9°); this (2.8 g.) and 30 ml. 48% HBr heated in sealed tube 12 hrs. at 120° gave 83% *4-(bromomethyl)thiazole HBr salt*, m. 209–9.5° (from EtOH). Heating 10 g. 2,4-dimethylthiazole and 5.8 g. I in 10 ml. CCl_4 15 min. to 60°, cooling, filtering, and washing the filtrate with dil. NaOH yielded 74% *2,4-dimethyl-5-bromothiazole*, b_{15} 75–80° (*picrate*, m. 104–5°). Similarly 20 g. 2,4,5-trimethylthiazole and 14.1 g. I in CCl_4 heated 15 min. at 60° gave 21.8% *2,5-dimethyl-4-(bromomethyl)thiazole*, b_{15} 88–90°, n^{20}_{D} 1.547, d^{20}_{20} 1.3383; *picrate*, m. 106.5–8°; HBr salt, m. 190–1°. Heating 3 g. 4,5-dimethyl-2-(hydroxymethyl)thiazole with 30 ml. 48% HBr in sealed tube 12 hrs. at 120°, followed by evapn. and treatment with K_2CO_3 gave an undistillable oil, which was converted with picric acid to *4,5-dimethyl-2-(bromomethyl)thiazole picrate*, m. 101.5–3°. Similarly, 2,4-dimethyl-5-(hydroxymethyl)thiazole gave 88.8% *2,4-dimethyl-5-(bromomethyl)thiazole HBr*, m. 194–5°. Cf. Tarbell, *et al.*, *C.A.* 40, 1070[illegible]

G. M. Kosolapoff

MIKHAYLOV, B.M.; PLATOVA, I.K.; PODKLETNOV, N.Ye.; GORSHTEYN, G.I; SILANT'YEVA, N.I.

Letters to the editor. Zhur. ob. khim. 27 no.3:833-834 Mr '57.
(Chemistry) (MLRA 10:6)

MIKHAYLOV, B.M.

Distr: 4E]3/4E2c(j)

Oxocyclotautomerism of di-2-hydroxyethylaminoacetone. B. M. Mikhailov and A. N. Makarova. *Zhur. Obshchei Khim.* 27, 1626-32(1957).—To 77 g. molten $NH(CH_2CH_2OH)_2$ was added over 1.5 hrs. 50 g. $BrCH_2Ac$ at 50° and after standing overnight, the mixt. was reheated to 50° 1 hr. and extd. with Et_2O, yielding 63% *2-methyl-2-hydroxy-4-(2-hydroxyethyl)morpholine* (I), m. 67-8°, which after rapid distn. b_4 135.5-6.5°, n_D^{20} 1.4847, d_{20} 1.1883; it reduces Fehling soln. and Tollens soln. in the cold and gives iodoform reaction; with semicarbazide it gave yellowish H_2NCO-$NHN:CMeCH_2NHNHCONH_2$, decomp. 253°; with H_2NOH it gives $MeC(:NOH)CH_2NHOH$, m. 163-4°. I in Et_2O with HCl gives HCl salt, m. 124-6°, which treated with EtOH yields some *2-methyl-2-ethoxy-4-(2-hydroxyethyl)morpholine-HCl* (II), m. 128-9°. I forms *methiodide*, m. 128-9°, while treatment of I with alc. HCl yields II, which with K_2CO_3 forms *free base* (III), b_2 101-1.5°, n_D^{20} 1.4683, d_{20} 1.0550, which does not reduce Fehling soln. in the cold, and with semicarbazide yields the same product as does I. III *methiodide*, m. 150-1°. III warmed with 20% HCl yields I. I with MeOH-HCl gave *2-methyl-2-methoxy-4-(2-hydroxyethyl)morpholine-HCl*, m. 125.5-6.5°. Repeated vacuum distn. of I gave a product, b_4 59-60°, n_D^{20} 1.4710, which changed on standing; treatment of this with HCl in Et_2O gave *2-methyl-4-(2-hydroxyethyl)-5,6-dihydro-1,4-oxazine-HCl*, m. 159-60°; *free base*, b_4 58.5-9°, n_D^{20} 1.4785, d_{20} 1.1168, m. 19° (IV); *methiodide*, m. 219-20°; *picrate*, m. 183-4°; *semicarbazide* yields the same product as formed from I. Refluxing the HCl salt in aq. soln. 1 hr. gave after treatment with K_2CO_3 90% I, while treatment with alc. HCl yields II. $NH(CH_2CH_2OH)_2$ with $BrCH_2Ac$ in dry EtOH gave in 1.5 hrs. 90% I, 25% III, and 35-40% IV.

G. M. Kosolapoff

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AUTHORS: Mikhaylov, B. M., Vaver, V. A.,

TITLE: Boron-Organic Compounds (Bororganicheskiye soyedineniya). Communication 22: On the Mechanism of Hydrolysis of Diarylboric Esters (Soobshcheniye 22: O mekhanizme gidroliza efirov diarilborn...)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 4, pp. 419-42? (USSR)

ABSTRACT: The alkylesters of diarylboric acids are ... the effect of hydr... as t... hydroxides of alkaline metals ... the ester of diarylboric acid ... diarylalkoxy... (see formula II) ... only to a small degree into diarylboric acid (formula IV) Mainly a cleavage of the elements of water ... takes place ... diaryl... Then a reco... the initial ... (see fo... The ... diarylboric acids ... very ... of ... in water ...

Card 1/2

Boron-Organic [illegible] lysis of Diaryl[illegible] Esters

[illegible] esters of diaryl[illegible] acid was [illegible] first reaction [illegible] of the esters of [illegible] acids form [illegible] hydrolysis [illegible] possibility [illegible] the ester [illegible] the complex with simultaneous formation of [illegible] borates of ammonium does not exist [illegible] be hydrolyzed (formulae VI, VIII, IX). A number of [illegible] of diarylboric acids and their [illegible] Further [illegible] Di-[illegible] acids and their derivatives were [illegible] There is 1 table, and 7 references, [illegible] Soviet.

Card 2/3

MIKHAYLOV, B.M.; VAVER, V.A.

Organoboron compounds. Report No.22 Hydrolysis mechanism of the diarylborates. Izv. AN SSSR Otd. khim. nauk no.4:425-427 Ap '58. (MIRA 11:5)

1. Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR. (Hydrolysis) (Boric acid)

62-58-5-3/27

AUTHORS: Mikhaylov, B. M., Kiselev, V. G., Bogdanov, V. S.

TITLE: Radiation-Chemical Conversions of Organic Substances (Radiatsionno-khimicheskiye prevrashcheniya organicheskikh veshchestv) Communication 3: Conversions of Ethylene Under the Action of Rapid Electrons (Soobshcheniye 3. Prevrashcheniya etilena pod vliyaniyem bystrykh elektronov)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 5, pp. 545 - 549 (USSR)

ABSTRACT: Mund and Kokh (Reference 2) investigated for the first time the radiation-action of high energy on ethylene. They found out that ethylene is converted into hydrogen under the influence of α-particles. Lind and his collaborators (Reference 3) obtained hydrogen and small quantities of methane and ethane by means of irradiation of ethylene by α-particles. Mak-Lennan and Patrik (Reference 4) discovered also acetylene besides H_2 and CH_4 in the reaction products of the radiolysis of ethylene. Moreover it was found that ethylene is con-

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62-58-5-3/27

Radiation-Chemical Conversions of Organic Substances. Communication 3: Conversions of Ethylene Under the Action of Rapid Electrons

verted into polyethylene or into liquid products on the action of γ-radiation. In the present work, the conversions of ethylene under the action of rapid electrons were investigated, as well as the influence of the irradiation-time of the initial pressure, the dilution of the initial ethylene by means of nitrogen and hydrogen. Gaseous and liquid reaction-products were subjected to the analysis. The authors found that the initial products of the radiolysis of ethylene do not represent hydrogen and methane, as was previously assumed, but butane and acetylene (References 2 to 4). The gaseous reaction-products contain, besides butane and acetylene, small quantities of C_2H_6, C_4H_8 and H_2, as well as traces of propylene. Liquid reaction-products (boiling out up to 130°C) consist of aliphatic hydrocarbons C_6 and C_8. The highest fractions contain important quantities of aromatic and unsaturated hydrocarbons. The formation of hexane, octanes of butane and other highest alkanes is carried out by means of the condensation of aliphatic biradicals and of an even number of carbon-atoms with subsequent hydration of the same. The energetic yield of reaction:

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Radiation-Chemical Conversions of Organic Substances. 62-58-5-3/27
Communication 3: Conversions of Ethylene Under the Action of Rapid Electrons

16 molecules per 100 eV. A reduction of the initial pressure increases the degree of decomposition of ethylene without influencing the course of reaction. A dilution of ethylene by means of nitrogen increases the conversion substantially (with intense reduction of the yield of gaseous hydrocarbons). A dilution by means of hydrogen does not influence the radiolysis of ethylene. There are 2 figures, 4 tables and 10 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute for Organic Chemistry imeni N.D. Zelinskiy, AS USSR)

SUBMITTED: February 8, 1957

1. Organic substances--Effects of radiation 2. Radiation--Chemical effects

Card 3/3

SOV/62-58-6-23/37

AUTHORS: Mikhaylov, B. M., Shchegoleva, T. A.

TITLE: On the Effect Produced by Primary Amines Upon the Esters of Alkyl-Chloroboric Acid (O deystvii pervichnykh aminov na efiry alkilkhlorbornykh kislot)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk 1958, Nr 6, pp. 777-779 (USSR)

ABSTRACT: In the present report the results obtained by the investigation of the effect produced by primary amines (of ethylamine and aniline) and upon alkyl-chloroboric acid are described. Under the action of these primary amines the esters of alkylchloroboric acids are transformed into esters of the alkylic boric acids and into N-substituted alkyl boron diamines (formulae I-IV). Reaction develops by way of the stage of amino-ester formation (IV). This ester is symmetrized either in ester and initial diamine or it reacts with the 2. alcohol molecule:

$$n\text{-}C_4H_9B(NHC_2H_5)_2 + ROH \rightarrow [n\text{-}C_4H_9BNHC_2H_5(OR)]$$

$$\downarrow ROH$$

$$n\text{-}C_4H_9B(NHC_2H_5)_2 + n\text{-}C_4H_9B(OR)_2 \text{ or } n\text{-}C_4H_9B(OR)_2 + C_2H_5NH_2$$

Card 1/2

On the Effect Produced by Primary Amines Upon the Esters of Alkyl-Chloroboric Acid

SOV/62-58-6-23/37

There is Soviet reference.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, AS USSR)

SUBMITTED: January 17, 1958

1. Alkyl chloroboric acid esters--Chemical reactions
2. Amines--Chemical reactions

Card 2/2

SOV/62-58-7-10/26

AUTHORS: Mikhaylov, B. M., Fedotov, N. S.

TITLE: Organic Boron Compounds (Bororganicheskiye soyedineniya) Communication 24. The Effect of Acetic Acid and Acetic Anhydride on Boron Phenyl Dichloride and Boron Diphenyl Chloride (Soobshcheniye 24. Deystviye uksusnoy kisloty i uksusnogo angidrida na fenilbordikhlorid i difenilborkhlorid)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 7, pp 857 - 859 (USSR)

ABSTRACT: The chemical properties of boron aryl dichlorides have been little investigated up to now. Mikhaelis systematically investigated the ratio between the boron aryl dichlorides and water, with which they react under the formation of boron aryl acids (Ref 1). Furthermore he investigated the effect of alcohol and chlorine (Refs 2,3) on boron phenyl dichloride as well as the effect of sodium methylate and ethylate on the β boron naphthyl dichloride. Still less information is available on the properties of the boron diaryl chlorides (Refs 5,6). In the present paper the formation of boron phenylpyro acetic anhydride by the action of acetic acid on boron phenyl dichloride is discussed. The authors found that boron diphenyl chloride reacts with acetic anhydride, with

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Organic Boron Compounds. Communication 24 The Effect of Acetic Acid and Acetic Anhydride on Boron Phenyl Dichloride and Boron Diphenyl Chloride

boron diphenyl anhydride being formed. Under the influence of acetic acid on boron diphenyl chloride first boron diphenyl anhydride is formed which lateron converts into boron phenyl-pyro acetic anhydride under the action of acetic acid. Boron p chlorophenyl dichloride reacts with acetic acid (under the simultaneous formation of chlorophenyl pyroacetic anhydride). There are 6 references 5 of which are Soviet.

ASSOCIATION Institut organicheskoy khimii im.N D.Zelinskogo Akademii nauk SSSR Institute of Organic Chemistry imeni N.D.Zelinskiy, AS USSR)

SUBMITTED December 28, 1956

SOV/62-58-7-11/26

AUTHORS: Mikhaylov, B. M., Shchegoleva, T. A.

TITLE: Organic Boron Compounds (Bororganicheskiye soyedineniya) Communication 25: On the Action of Organic Acids on the n.Butyl Esters of n.Chloro Propyl Boric Acid (Soobshcheniye 25. O deystvii organicheskikh kislot na n.butilovyy efir n.propilkhlorbornoy kisloty)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 7, pp 860 - 865 (USSR)

ABSTRACT: The properties of the esters of chloro aryl boric acids and chloro alkyl boric acids (produced by means of the interaction of equimolecular amounts of esters or organoboric acids and phosphorus pentachloride) (Refs 1,2) have hitherto been little investigated. In the present paper the results of the investigation of the reactions between the n.butyl ester of chloro propyl boric acid and organic acids is discussed. On the action of acetic acid on the butyl ester of chloro propyl boric acid the n.butyl esters of n.butyl boric acid, n.boron propyl pyroacetic anhydride, chlorobutyl and butyl acetic ester are formed. By the action of propionic acid on the n.butyl ester of the

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SOV/62-58-7-11/26

Organic Boron Compounds. Communication 25: On the Action of Organic Acids on the n.Butyl Esters of n.Chloro Propyl Boric Acid

n.chloro propyl boric acid the n.butyl ester of n.propyl boric acid, n.boro propyl pyro propionic anhydride, chlorobutyl and butyl ester of propionic acid are formed. The authors also explained the mechanism of the reactions between organic acids and the ester of n.chloro propyl boric acid. The n.butyl ester of n.propyl boric acid reacts with acetic anhydride in the presence of hydrogen chloride with a simultaneous formation of n.boron propyl pyro acetic anhydride, butyl acetic ester, chloro butyl and chloro acetyl. There are 6 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im.N.D.Zelinskogo Akademii nauk SSSR(Institute of Organic Chemistry imeni N.D.Zelinskiy, AS USSR)

SUBMITTED: December 23, 1956

Card 2/2

APPROVED FOR RELEASE: 07/12/2001 CIA-RDP86-00513R001034010002-0"

APPROVED FOR RELEASE: 07/12/2001 CIA-RDP86-00513R001034010002-0"

MIKHAYLOV, B. M.

[illegible]-1-2/20

AUTHORS: Nikitina, A. N., Galanin, [illegible], Aronovich, P. M., Shchegoleva, T. A., Mikhaylov, [illegible]

TITLE: An Investigation of Boron Organic [illegible] lators (Issledovaniye stsintillyatorov, [illegible] ganicheskiye soyedineniya)

PERIODICAL: Izvestiya AN SSSR Seriya Fizicheskaya, 1958, Vol. 22, Nr 1, pp. 12-15 (USSR)

ABSTRACT: The authors investigated a number of organoboron compounds [illegible] of them were for the first time obtained in reference 3) for the purpose of determining the possibility of using them for the recording of slow neutrons. The esters of alkyl- and [illegible] boric acid were investigated on teir introduction into a liquid scintillator - a p-terphenyl-solution. It became evident that the intensity of the γ-scintillation of the latter does almost not change. Triethylborate used in the practice of nuclear [illegible] weakens the γ luminescence of the p-terphenyl-solution [illegible]. It is shown that the esters of aryl- and diarylboric acid on their introduction into a p-terphenyl-solution cause a considerable weakening of the scintillation of the latter [illegible]. The organoboron compounds with aryl-substituents the solvent [illegible] a weak γ-luminescence.

Card 1/2

An Investigation of Boron Organic Compounds Containing Scintil- [illegible]
lators.

There are 1 table, and 6 references, 3 of which are [illegible].

ASSOCIATION: Institute for Organic Chemistry imeni N.D. Zelinskiy AS USSR (Institut organicheskoy khi [illegible] AN SSSR). Institute for Physics imeni P.N. Lebedev AS USSR (Fizicheskiy institut im. P.N. Lebedeva AN SSSR)

AVAILABLE: Library of Congress

1. Chemistry 2. Boron compounds-Application

Card 2/2

MIKHAYLOV, B.M.

NIKITINA, A.N.; GALANIN, M.D.; ARONOVICH, P.M.; SHCHEGOLEVA, T.A.; MIKHAYLOV, B.M.

Analysis of scintillators containing boron organic compounds. Izv. AN SSSR. Ser. fiz. 22 no.1:14-20 Ja '58. (MIRA 11:2)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR i Fizicheskiy institut im. P.N. Lebedeva AN SSSR.
(Scintillation counters)
(Nuclear physics--Instruments)

MIKHAYLOV, B. M.

-1-31/13

AUTHORS: Mikhaylov, . . , Makarova, A. N.

TITLE: The Condensation of ω-Bromacetophenone With Diethanolamine (O kondensatsii ω-bromatsetofenona s dietanolaminom).

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol 28, Nr . , pp. 150-1.3 (USSR).

ABSTRACT: It was of interest to investigate the properties of the condensation product of ω-haloidacetophenone with diethanolamine and to find out whether it actually possesses a chain structure as suggested by Brighton and Reid (reference .) or whether it represents a cyclic compound. In order to synthesize this product the ethereal solution of ω-bromacetophenone was added to diethanolamine. The smooth reaction led with a good yield to a compound with a melting point of 77-78° C (not 44° C as indicated). It was determined that it is no oxyaminoketone (formula I) but its tautomeric form a cyclic semiacetate, i.e. a 2-phenyl-2-oxy-4-β-oxyethylmorpholine (II) (see formulae). Compound (II) easily changes already at room temperature; it turns yellow or becomes resinous. The hydrate obtainable by recrystallization in water loses the water again on heating. The hydrochloride of the semiacetal (II) is by the influence

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79-1 31/43

The Condensation of ω-Bromacetophenone With Diethanolamine

of anhydrous ethyl alcohol converted to the hydrochloride of acetal-2-phenyl-2-ethoxy-4-β-oxy-ethylmorpholin (III R = C_2H_5) which by naturalization with potash easily leads to the base. The hydrochloride of the acetal hydrolizes at 70°C under the formation of semiacetal. The acetal (III) was liberated from the hydrochloride by potash and characterized as iodomethylate and picrate. Semiacetal does not lead to any semicarbazone. By the influence of semicarbacide upon it a solid body with much nitrogen is obtained, which is also the case with acetal. With some reagents semiacetal reacts like a typical α-aminoketone. Thus it rapidly reduces Fehling's solution and the ammonia solution of silver oxide. In contrast to acetal (III). On heating with concentrated hydrochloric acid semiacetal splits off water and is converted to 2-phenyl-4-β-oxyethyl-5,6-dihydroxazine-1,4 (IV). There are 5 references, 1 of which is Slavic.

ASSOCIATION: Institute for Experimental Pathology and Cancer Therapy (Institut eksperimental'noy patologii i terapii raka).

SUBMITTED: January 2, 1957

AVAILABLE: Library of Congress

Card 2/2

1. Chemistry 2. Cyclic compounds-Condensation

MIKHAYLOV, B.M.

7--.-17/4

AUTHORS: Mikhaylov, B. M., Kurdyumova, K. N.

TITLE: Structure and Chemical Conversions of Organic Alkali Compounds of Anils (Stroyeniye i khimicheskiye prevrashcheniya ... neorganicheskikh soyedineniy anilov)
III. On the Conversions of Disodium- and Dilithium-Compounds of Benzophenone-o-Tolylimide and Benzophenone-p-Tolylimide Under the Influence of Alkyl Halide (III. O prevrashcheniyakh dinatriyevykh i dilitiyevykh soyedineniy benzofenon-o-tolilimida i benzofenon-p-tolilimida pod vliyaniyem galoidnykh alkilov)

PERIODICAL: Zhurnal Obshchey Khimii, 1 5 , Vol , Nr , pp. - (USSR)

ABSTRACT: In the preceding information (reference 1) it was ... that the influence of alkyl halide upon metallic compounds of benzophenonphenylimide ... complicated conversions. As a result ... the alkahydrilamine - a product of substitution ... of the metal by hydrogen atoms - and a number of substances forming due to the molecule-decomposition according to the carbon-nitrogen linkage are obtained: aniline, phenylated ethylenic hydrocarbons, ...,2,3,3,-tetraphenylbutane (with the use of alkyl halide) as well as gaseous hydrocarbons. For determining the influence exerted by the aryl radical structure on the nitrogen atom upon the course of

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79-2-17/31

Structure and Chemical Conversions of Organic Alkali Compounds of Anils. III. On the Conversions of Disodium- and Dilithium-Compounds of Benzophenone- -Tolylimide and Benzophenone-p-Tolylimide Under the Influence of Alkyl Halides

the reaction of dimetallic anil compounds the authors investigated the action of methyl iodide and methyl chloride upon disodium- and dilithium-compounds of benzophenone-o-tolylimide and benzophenone-p-tolylimide. ... leading to the formation of ... various substances ... observed in the interaction of the dilithium compound of benzophenone-o-tolylimide and methyl iodide. The production of ... compounds of benzophenone-o-tolylimide and benzophenone-p-tolylimide were performed under the same conditions as they were described for organic metal compounds of benzophenone... (reference 1). Conclusions: 1) The presence and position of the ... group in the aryl radical at the nitrogen ... of the ... ine ... exert considerable influence upon the course of the process under the action of the methyl halides upon dimetallic benzophenone-o-tolylimide- and benzophenone-p-tolylimide-derivatives. ... Under influence of methyl-iodide dimetallic benzophenone-o-tolylimide derivatives can substitute metal atoms ... with the formation of the secondary amine - ...-tolyl-1,1-diphenylethylamine and the tertiary amine - methyl-o-tolyl-1,1-diphenylethylamine. Simultaneously with the formation of amines one can observe the splitting of the azomethine bond in the dimetallic derivative and the formation of o-toluidine, 1,1-diphenyl-

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79-2-17/64

Structure and Chemical Conversions of Organic Alkali Compounds of Anils. III. On the Conversions of Disodium- and Dilithium-Compounds of Benzophenone-o-Tolylimide and Benzophenone-p-Tolylimide Under the Influence of Alkyl Halide

ethylene and 2,2,3,3-tetraphenylbutane. 3) Under the influence of the methyl halide upon dimetallic benzophenone-p-tolylimide derivatives and under the simultaneous formation of the tertiary amine - methyl-p-tolyl-1,1-diphenylethylamine - the splitting of the C - N bond in the dimetallic derivative and the formation of p-toluidine, 1,1-diphenylethylene and 2,2,3,3-tetraphenylbutane is observed. There are 1 table, and 4 references, 2 of which are Slavic.

SUBMITTED: April 20, 1957

AVAILABLE: Library of Congress

Card 3/3

AUTHORS: Mikhaylov, ~~B. M.,~~ Kozminskaya, T. K. SOV/20-121-4-23/54

TITLE: The Effects of Amines and Ammonia on Boron Isoamyl Dichloride (O deystvii aminov i ammiaka na izoamilbordikhlorid)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 121, Nr 4, pp. 656 - 659 (USSR)

ABSTRACT: The process of the reactions taking place between boron phenyl dichloride and amines depends on the nature of the amine. It was therefore of interest to investigate the behaviour of boron alkyl dichlorides towards amines and ammonia. In the case of an action of ethylamine isoamyl borodichloride is changed to isoamyl-bis(ethylamino) boron (I) and B-tri-isoamyl-N-triethyl borazole (II). The reaction with isobutyl amine proceeds in an analogue way; a) isoamyl-bis (isobutylamino) boron (I) and b) B-tri-isoamyl-N-isobutyl borazole (II) are formed. In the first stage apparently alkyl alkylamino chloric boron (III) which then enters the reaction with a further amine molecule; it forms (I) and is condensed to borazole (II). In the case of aniline action boron isoamyl dichloride forms boron (IV) isoamyl-bis (phenylamine). In a good yield the latter

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The Effects of Amines and Ammonia on Boron Isoamyl Dichloride SOV/20-121-4-23/54

is changed to B-tri-isoamyl-N-phenyl borazole (V) which is a representative of the up to now unknown B-trialkyl-N-triaryl borazoles. The reaction between boron isoamyl dichloride and diethylamine proceeds under formation of boron (VI) isoamyl-bis (diethyl amine). When ammonia is flown through an ether solution of boron isoamyl boron-dichloride B-tri-isoamyl borazole (VII) is formed. An experimental part containing the usual data follows. There are 7 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im.N.D.Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N.D.Zelinskiy, AS USSR)

PRESENTED: April 4, 1958, by B.A.Arbuzov, Member, Academy of Sciences, USSR

SUBMITTED: March 25, 1958

Card 2/2

5(2,3)

SOV/20-123-3-27/54

AUTHORS: Mikhaylov, B. M., Tutorskaya, F. B.

TITLE: Organoboron Compounds (Bororganicheskiye soyedineniya) Allyl Derivatives of Boron (Allil'nyye proizvodnyye bora)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 3, pp 479-482 (USSR)

ABSTRACT: From among the allyl compounds of boron only triallyl boron is well known. The data of reference 1 on the synthesis of other compounds of this series are to be noticed with reservation, according to the opinion of the authors. But the authors have obtained, apart from the investigation of the chemical properties of triallyl boron, a number of new allyl derivatives of boron. Triallyl boron is far more reactive than the boron trialkyl compounds. It reacts with water already at room temperature. Allyl boric acid is formed therein which was isolated as an anhydride. Triallyl boron reacts also with alcohols at room temperature. Under the influence of one mol n-butyl alcohol the n-butyl ester of diallyl boric acid is formed under propylene separation. Under the influence of methyl alcohol no methyl ester of this acid but the dimethyl ester of allyl boric acid

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Organoboron Compounds. Allyl Derivatives of Boron SOV/20-123-3-27/54

is formed, whereas part of the initial triallyl boron is recovered unchanged. The esters of diallyl boric acid are very unstable against water: under the influence of water they are hydrolyzed even in the cold to allyl boric acid. The authors criticize the data of reference 1 and prove that those investigators cannot have obtained the anhydride of diallyl boric acid nor the methyl ester of this acid nor any compound with a boiling-point of $110^{\circ}/0.4$ mm. Triallyl boron readily reacts with n-butyl amine at room temperature, which yields diallyl-n-butyl-amino-boron at an identical molecular ratio. The products of the reaction between allyl magnesium bromide and trimethyl borate contain dimethyl esters of allyl boric acid and triallyl boron in the weak distillate (if the reaction products are not decomposed by water). After decomposition by dilute HCl and esterification by allyl alcohol the diallyl ester of the allyl boric acid was formed. Due to the influence exerted by allyl magnesium bromide upon the n-butyl ester of the meta-boric acid with subsequent decomposition of the products by water and esterification by n-butyl alcohol, the dibutyl ester

Card 2/3

Organoboron Compounds. Allyl Derivatives of Boron SOV/20-123-3-27/54

of the allyl boric acid and a substance with boiling-point 166°/2.5 mm with an identical elementary composition but with a double molecular weight result. The structure of this dimer is unknown. An experimental section with the usual data follows. There are 4 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

PRESENTED: July 11, 1958, by B. A. Kazanskiy, Académician

SUBMITTED: July 11, 1958

Card 3/3

SOV/62-59-1-12/38

5(3)

AUTHORS: Mikhaylov, ~~B. M.~~, Bazhenova, A. V.

TITLE: Organo-Boron Compounds (Bororganicheskiye soyedineniya) Communication XXIX. Cyclohexylboric Acid and Its Derivatives (Soobshcheniye 29. Tsiklogeksilbornaya kislota i yeye proizvodnyye)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 76 - 79 (USSR)

ABSTRACT: Among organo-boron compounds of the alicyclic series only tricyclohexyl boron is known. It was obtained by Krause and Polack by the action of halide cyclohexyl magnesium on boron fluoride (Ref 1). In the present paper the authors obtained the ester of cyclohexylboric acid by the action of cyclohexyl magnesium chloride on trimethyl borate. In the interaction of equimolecular quantities of the isobutyl ester of cyclohexylboric acid with phosphorus pentachloride the ester of cyclohexylchloroboric acid is formed. By the action of 2 mols phosphorus pentachloride on the ester of cyclohexylboric acid cyclohexyl boron dichloride is formed. By the action of 1 mol water on 2 mols ester of the cyclo-

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Organo-Boron Compounds. Communication XXIX. Cyclohexyl- SOV/62-59-1-12/38
boric Acid and Its Derivatives

hexylchloroboric acid the ester of cyclohexylboric acid and the cyclohexylboric acid anhydride are formed. By the action of water on the latter the corresponding acid was obtained. There are 4 references, 3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: April 19, 1957

Card 2/2

5(3)

SOV/62-59-1-13/38

AUTHORS: Mikhaylov, B. M., Kozminskaya, T. K.

TITLE: Organo-Boron Compounds (Bororganicheskiye soyedineniya) Communication XXX. Organo-Boron Compounds of the Pyridine Series(Soobshcheniye 30. Bororganicheskiye soyedineniya piridinovogo ryada)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 80 - 84 (USSR)

ABSTRACT: Among the organo-boron compounds containing heterocyclic radicals only the α-thiophene boron and α-furyl boric acid are known. They were obtained by the effect of Grignard's reagents upon methyl borate (Ref 1). The authors investigated the influence of α-pyridyl lithium and α-picolyl lithium upon triisobutyl borate in order to obtain organo-boron compounds of the pyridine series. It was found that by the effect of α-pyridyl lithium or α-picolyl lithium upon triisobutyl borate corresponding lithium salts of the α-pyridyl triisobutoxy boric acid and α-picolyl triisobutoxy boric acid are formed. By the influence of hydrochloric acid upon the compounds obtained pyridine or α-picoline and boric

Card 1/2

Organo-Boron Compounds. Communication XXX. Organo-Boron Compounds of the Pyridine Series SOV/62-59-1-13/38

acid or their esters are obtained accordingly. By the influence of water upon α-pyridyl- and α-picolyl triisobutoxy boric acid the isobutoxyl ester groups are saponified. Corresponding α-pyridyl- or α-picolyl boric acids are formed thereby. On boiling α-pyridyl or α-picolyl boric acids with alcohol an esterification of the hydroxyl groups in the complex anion takes place. Corresponding salts of the α-pyridyl- or α-picolyl triisobutoxy boric acids are formed. There are 4 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: April 27, 1957

Card 2/2

S V/62-59-1-32/39

5(3)

AUTHORS: Mikhaylov, B. M., Bubnov, Yu. N.

TITLE: Synthesis of the Esters of Dialkyl Thioboric Acids and Their Transformations (Sintez efirov dialkiltiobornykh kislot i ikh prevrashcheniya)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 172 - 173 (USSR)

ABSTRACT: In this communication the authors report on the investigation of the reactivity of boro trialkyls with sulfur. The experiments have shown that tri-n-propyl boron or tri-n-butyl boron react with sulfur on heating (145°) and accordingly form n-propyl esters of the di-n-propyl thioboric acid as well as n-butyl esters of the di-n-butyl thioboric acid. The esters of dialkyl thioboric acid are highly reactive compounds. By the action of water they are hydrolized in dialkyl boric acids. By the reaction of alcohol they are transformed into esters of the dialkyl boric acids. Esters of dialkyl thioboric acids readily react with amines and are transformed into N-substituted dialkyl boron amines. By the action of hexamethylene diamine they are transformed

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into N,N'(didialkyl-boryl)-1,6-diamino-hexanes. With ammonia they form dialkyl boron amines. By the action of hydrazine the thioesters are transformed into 1,2-di-(dialkyl-boryl) hydrazines. There are 4 references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: June 17, 1958

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SOV/62-59-2-20/40

5(3)

AUTHORS: Mikhaylov, B. M., Povarov, L. S.

TITLE: Polyenic Compounds (Poliyenovyye soyedineniya). Communication 3. New Method of Synthesis of Diarylpolyenic Hydrocarbons (Soobshcheniye 3. Novyy metod sinteza diarilpoliyenovykh uglevodorodov)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk. 1959, Nr 2, pp 314-319 (USSR)

ABSTRACT: This paper presents a new general method for the synthesis of diphenylpolyenic hydrocarbons. This method is based on the utilization of condensation products of the acetal-benzaldehyde with vinyl ether. On the action of benzyl magnesium chloride on phenyl polyethoxy-alkane $C_6H_5\left[\begin{matrix}CH-CH_2-\\ |\\ OC_2H_5\end{matrix}\right]_n-CH(OC_2H_5)_2$

diphenyl polyethoxy-alkanes are formed $C_6H_5\left[\begin{matrix}CH-CH_2\\ |\\ OC_2H_5\end{matrix}\right]_{n+1}-C_6H_5$

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The latter are transformed under the influence of aqueous alcoholic hydrogen bromide solution into the diphenylpolyenic hydrocarbons. When benzyl-magnesium chloride is acting on phenyl ethoxy-aldehydes $C_6H_5\left[\begin{array}{c}CH-CH_2\\ |\\ OC_2H_5\end{array}\right]_n-CHO$

diphenyl oxy-polyethoxy-alkanes are formed

$$C_6H_5\left[\begin{array}{c}CH-CH_2\\ |\\ OC_2H_5\end{array}\right]_n\begin{array}{l}-CH-CH_2-C_6H_5\\ \ \ \ |\\ \ \ OH\end{array}$$

These are transformed into diphenylpolyenic hydrocarbons under the influence of aqueous alcoholic hydrogen bromide solution. There are 6 references, 1 of which is Soviet.

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SOV/62-59-2-30/40

5(3)

AUTHORS: ~~Mikhaylov, B. M.,~~ Shchegoleva, T. A.

TITLE: Effect of Selenium on Boron Trialkyls (Deystviye selena na bortrialkily)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1959, Nr 2, pp 356-357 (USSR)

ABSTRACT: In the present news in brief the authors report on the behavior of boron trialkyls towards selenium. It was found that they react with selenium in a very peculiar way. On heating of the mixture of tri-n-butyl boron and selenium a gradual decomposition of selenium was observed at 220-250° which is accompanied by an intense separation of gaseous products. As a result of the reaction $C_8H_{18}B_2Se_3$ is formed. On the hydrolysis of this compound n-butyl boric acid was precipitated which indicates the occurrence of a B-C bond. It is assumed that the compound obtained has a cyclic structure (Ref 1). According to the rules for the nomenclature of saturated 5-membered heterocyclic systems (Ref 3), this compound was called 3,5-di-n-butyl-3,5-diboron-1,2,4-triselenolane. The gas separated during the re-

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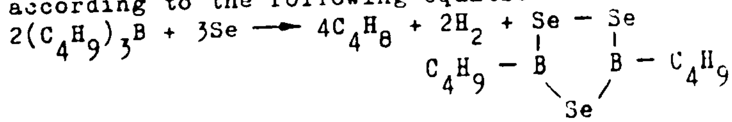
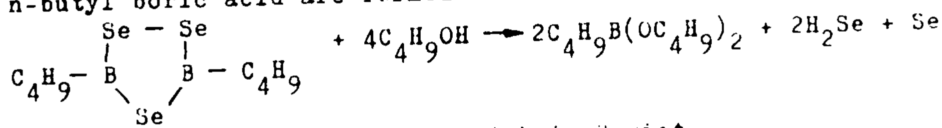
action contains hydrogen and butylene. The reaction proceeds according to the following equation:



A similar reaction takes place on heating of triisobutyl boron with selenium, wherein 3,5-diisobutyl-3,5-diboron-1,2,4-triselenolane (II) is formed. 3,5-dialkyl-3,5-diboron-1,2,4-diselenolanes are yellow viscous liquids. They are very sensitive to atmospheric moisture and oxygen. By the influence of n-butyl alcohol upon 3,5-di-n-butyl-3,5-diboron-1,2,4-triselenolane metallic selenium, hydrogen selenide and n-butyl esters of the n-butyl boric acid are formed.



There are 3 references, 1 of which is Soviet.

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ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: July 9, 1958

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5(3)

AUTHORS: Mikhaylov, B. M., Shchegoleva, T. A. SOV/62-59-3-25/37

TITLE: Synthesis of Trialkyl Borons With Functional Substituents (Sintez bortrialkilov s funktsional'nymi zamestitelyami)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 3, pp 546-547 (USSR)

ABSTRACT: This is a brief communication on the investigation of the reaction of diborane with vinyl-ethyl ether. Tri-(2-ethoxy-ethyl)-boron (I) was obtained in insufficient purity as a result of this reaction. Probably, in this case the reaction is complicated by side reactions. In reference 6 it was shown that the lowest alkyl group may be easily replaced by the highest one if the mixture of the corresponding trialkyl boron and olefin is heated and the easily volatile olefin is removed from the reaction mixture. The authors extended this reaction to unsaturated compounds with functional substituents. By heating triisobutyl boron with 2-chloro-1,1,2-trifluoroethyl allyl ether (II) tri-[3-(2'-chloro-1',1',2'-trifluoroethoxy)propyl] boron (III) was obtained in a yield of 52 %. Triisobutyl boron reacts also with unsaturated organosilicon compounds. By heating triisobutyl boron with allyl trimethyl silane or

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allyl trichlorosilane tri-(3-trimethyl silyl propyl) boron (IV) and tri-(3-chlorosilyl propyl)boron (V) were obtained accordingly in yields of 62-69 %. The investigations of the synthesis of functional trialkyl boron derivatives according to the mentioned method are continued. There are 7 references, 1 of which is Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

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